The George Fisher Baker
Non-Resident Lectureship in Chemistry
At Cornell University

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THE GEORGE FISHER BAKER
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VOLUME 4

Salts, Acids, and Bases: Electrolytes: Stereochemistry

by

PAUL WALDEN

THE GEORGE FISHER BAKER
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Salts, Acids, and Bases: Electrolytes: Stereochemistry

BY
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TO MY COLLEAGUES IN THE DEPARTMENT
OF CHEMISTRY OF CORNELL UNIVERSITY IN
SINCERE REGARD AND GRATITUDE

68900

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PREFACE

These lectures were delivered at Cornell University during the First Semester of 1927–1928 under the Non-Resident Lectureship in Chemistry endowed by Mr. George Fisher Baker.

The lectures deal with the three fields of scientific work in which I have been especially interested, the History of Chemistry, Electrochemistry, and Stereochemistry. They were written in German and were then translated into English by Dr. L. F. Audrieth, and I wish here to express my heartfelt appreciation of his patient, industrious, and skillful collaboration.

I shall always remember with delight the kindness of Professor Dennis and his colleagues, beautiful Cornell, and the Baker Laboratory.

INTRODUCTORY LECTURE

WHAT CAN THE MODERN CHEMIST LEARN FROM THE OLD ALCHEMY?

IT WAS with very sincere pleasure that I accepted appointment to the Non-Resident Lectureship in Chemistry at Cornell for the coming term. I keenly appreciate the honor of the invitation, not only because it gives me opportunity of being a teacher in this famed university, but also, and even more, because of what I can here learn, for it is with us men of science from Europe as it was in the early days with the philosophers of old Greece, a Plato, or a Pythagoras: they journeyed as wise men to Egypt and returned as students of the wisdom of the Egyptian priests.

Indeed, to learn and to work in such an ideal laboratory as the Baker Laboratory of Chemistry is for every chemist, whether old or young, an actual joy. This monumental Temple of Science not only has the best equipment, but a master of the art, the head of the department of chemistry, has furnished it with light and air. A German once has said of the Chemical Laboratory in Munich: "In diesem Hause stinkt es sehr, Dies kommt von Adolf Baeyer her." The Baker Laboratory of Chemistry is exceptional in this regard, it is the most odorless laboratory of the world; it has *no* smell.

The subject which I have chosen for this introductory lecture is: "What can the modern chemist learn from the old alchemy?"

By some this question may be received with astonishment, while others may raise energetic protest. What? We modern chemists, the witnesses and workers of this "Age of Chemistry," can learn something from the old alchemy, full as it was of errors and fantasies! The daily press is constantly announcing the startling results of scientific

research: "The riddles of the world are solved!" . . . "The proton has been isolated!" . . . "Atoms have been decomposed!" . . . "The chemical elements have been changed one into another!" . . . "The philosopher's stone has finally been found!" . . . "The transmutation of cheap elements into gold has been accomplished and patented," etc., etc. It almost seems as if we chemists were on the direct road to become God-like and all-powerful, but if we actually were so all-powerful, what would there be left for us to learn, and how could we control the enormous forces which we had developed?

In the days of the old alchemy there flourished in Italy a poet, Augurelli, who presented in 1518, in hexameter, to Pope Leo X, a work upon the "*Chrysopoeia*," or the true art of making gold. As a reward the Pope presented to this possessor of the Philosopher's Stone an empty purse, since to a man who possesses the secret, nothing is lacking except a purse in which to place and keep the artificially prepared metal.

The Past and the Present! Let the Past furnish us a warning aginst too much phantasy in modern chemistry.

Let us examine with the magnifying glass of time the development of chemistry through separate characteristic periods of the past, in an attempt to see more clearly the relationship between the science of to-day and that of the "good old times" which have largely been forgotten. In this glance backward, we will consider first the old chemists as men and as the so-called "Fathers of Chemistry;" second, the methods of work of the old chemists, experiments or sophistry; third, the problems and the goal of the old chemistry; and fourth, the purification of matter then and to-day—the purity of matter as a fundamental problem of the chemistry of the future.

I. THE OLD CHEMISTS AS MEN, AND THE SO-CALLED "FATHERS OF CHEMISTRY"

Seven cities once claimed to be the birthplace of the renowned Homer. But while place and time of this gifted poet's birth are veiled in obscurity, his name and writings

endure. And so is it with the origin and the name of Chemistry. Think of the many terms which were applied to the science—Egyptian, Holy, Hermetic Art, Poiesis, Scientia Alchimiae, etc. And yet the name *Chymia* means nothing further than cast metal, and Chymie, the art of casting metals.[1]

Where was the birthplace of this Chymie? Who were its founders? Some ascribe its origin to Egypt, others to India and China, others, more recently, to Babylon and Assyria. A fourth group of historians find the beginnings of the *science* in classic Hellas, while still others give to the Arabians the credit for the *practical* development of chemistry. And thus we see the mythical Hermes Trismegistos hailed as the seer of magic and chemistry, Empedocles as the father of the theory of the elements, Democritus as the originator of the atomic theory, Geber as the father of alchemy. Paracelsus is honored as the father of iatrochemistry and Masson has recently bestowed upon Robert Boyle the comprehensive title, "The Father of Chemistry."[2] Some of you are also acquainted with the judgment of Wurtz[3]—"La chimie est une science française, elle fut constituée par Lavoisier," and toward the end of the nineteenth century Grimaux[4] stated, "Toute la science moderne n'est que le developpement de l'oeuvre de Lavoisier."

We will not seek to decide which of these pioneers is entitled to the greater credit or whether the striking advances in the beginning of our science are due jointly to Boyle with Becher and Glauber, or to Lavoisier with Stahl, or to Priestley, or Scheele, or to Cavendish. Nor can the development of "toute la chimie moderne" be ascribed to a Dalton or an Avogadro, a Davy, a Berzelius or a Faraday. No single man is entitled to be called the "father of chemistry." And to those who seek to give this title to any single man the terse instruction in the Civil Code of Napoleon might be quoted, "La recherche de la paternité est interdite." Let us not be so narrow-minded as to at-

[1] Diels, *Antike Technik*, p. 124 (2nd Ed., 1920).
[2] Masson, *Three Centuries of Chemistry*, p. 57 ff. (London, 1925).
[3] Wurtz, *Histoire des doctrines chimiques*, 1868.
[4] Grimaux, *Lavoisier*, p. 128 (Paris, 1896).

tempt to proclaim any one single man as the "father of chemistry," but rather let us regard the development of the science as the product of the combined intellects of the men of all times and of a universal search for the truth.

Let us go back to the time of a Paracelsus and the beginning of iatro-chemistry. Chemistry which up to that time had been primarily directed along metallurgical lines, underwent decided change in character: *Man* himself, and his diseases, became the chief subject of chemistry. The physician becomes chemist, and accordingly a benefactor of mankind. The knowledge of the iatro-chemist was sought in all countries and at all of the higher institutions of learning, such as Padua, Bologna, Paris and Montpellier, or Leyden, Basle, Prague, Wittenberg and Leipzig. Many incidents in the history of chemistry witness the noblest sort of competition, the highest degree of internationalism and political tolerance, as well as recognition of individual merit. Take the case of the famous French chemist, the demonstrator of chemistry at the *Jardin des Plantes* in Paris, Nicholas Lefebvre, who in 1664 was called to London to take charge of the laboratory of St. James; or that of Wilhelm Homberg (died 1715), successively German lawyer in Magdeburg, medical student in Padua and student of chemistry under Boyle in London, then doctor of medicine at Wittenberg, personal physician to the Duke of Orleans in Paris, finally becoming a noted chemist and a member of the Paris Academy; or Becher, who was successively professor of medicine at Mayence (1666), then director of the laboratory in Munich, member of the Chamber of Commerce in Vienna, in practice at Haarlem and at last in 1680 in England where he examined the Scottish lead mines and smelting works and in 1681-1682 visited Cornwall and "studied the mines and smelting works . . . here he suggested several improvements and ameliorations."[1]

In the olden times a certain privileged freedom prevailed in the practice of the chemical and medico-chemical callings. Knowledge opened the doors to all classes of

[1] Thomson, *History of Chemistry*, I, p. 247 (1830).

European culture of that time. This knowledge flowed through the whole world like a liquid. It created a spiritual unity among scholars, and paved the way for mutual understanding among the nations and a joint cultural development. Consequently the practical chemist and medical chemist of whatever nation became an international carrier of culture and an apostle of peace.

What about to-day? Must it be so altogether different? If I may be permitted to express my opinion with reference to the creation of the Non-Resident Lectureship here at Cornell, it is this. The value of such an arrangement lies not alone in the scientific and pedagogic activity of the temporary incumbents in their special fields, but further than that, it serves to renew these old and highly ethical forms of reciprocal contacts between scientists in order to create a mutual spiritual atmosphere, and to pave the way for a peaceful cultural development of mankind. From this point of view the step taken by Cornell University may be regarded as historically significant. By her action the great traditions of science become alive again, and we are all moved by the spirit which led Humphry Davy to state publicly one hundred years ago, "Science, like that Nature to which it belongs, is neither limited by time nor space; it belongs to the world and is of no country and of no age."

II. THE WORKING PRINCIPLES OF THE OLD CHEMISTS. EXPERIMENT OR SOPHISTRY?

Thou, youthful seeker after knowledge, investigate and experiment and never desist therefrom, for thou shalt harvest fruits a thousand fold.—*Geber.*

These were the words of the famous Arabic encyclopedist of the old chemistry, the mythical Geber, some seven hundred years ago. "Labora, ora et—invenies" . . . did the "adepts" in the monastic cells call out in the middle ages. From among the ranks of the iatro-chemists, we are cautioned at the beginning of the seventeenth century "Alchemy is not attained without work" (that is, experiment).[1]

[1] Crollius, *Basilica Chymica* (1629).

It is a fact that this uninterrupted work, this indefatigable research has broadened and deepened chemical knowledge. "Desist not therefrom, for thou willst harvest fruits a thousand fold," so spoke the experienced practician Geber. Are we not struck with awe when contemplating this old experimental art, which after centuries of endeavor finally succeeded in preparing hydrochloric acid from salt and clay, nitric acid from saltpeter and clay, sulphuric acid from calcined vitriol or alum, and were able with these acids to obtain the key to analysis and synthesis? Think how long these experimental methods took, as compared with the methods of preparation employed in our modern procedure. Only experiment brought the thousand-fold fruits. Very often the latter were not even anticipated by the investigator. They came accidentally. We can, therefore, understand the lesson which Liebig, famous both as a discoverer and experimental artist, gave a hundred years ago. "If one works, one is always certain to make discoveries, it makes no difference where one begins."

Any scientific work may lead to a discovery. A pregnant thought. More remarkable, however, are oftentimes the conditions, in particular the mental conditions, under which such a task proceeds. Let us take, for instance, such a divinely gifted discoverer as Sir Humphry Davy (1778-1829). After he had attained world fame, in 1807, by his discovery of alkali electrolysis, it was necessary for him to appear in society more often than he wished. Despite this, he always went to his laboratory after he had returned to his home, where he continued to work until three or four o'clock in the morning. His biography states . . . "His greatest lack was that of time. He was forced to hurry . . . he would put on clean clothes without removing the soiled ones . . . at times he would have on as many as five shirts and several pairs of socks over one another. He would often arouse astonishment among his friends with the speed at which his corpulence increased and decreased." It has jokingly been said that Davy's greatest discovery was Faraday. Faraday, an unusually

gifted man, wrote of his work (1845), "I am so engrossed in discoveries that I have barely time enough to eat."

There is another, in whom literature and science in unique combination led to great results. Goethe, the famous poet, creator of *Faust*, was also a great natural scientist. After he had discovered the middle jaw bone in man, *Os intermaxillare*, in 1784, he wrote in a letter, "It has become a delightful avocation for me; I have made an important and pretty anatomical discovery, and I am so happy that my internal organs dance."

Here Goethe has succinctly revealed the psychological principles of work and discovery. It is the joy in the progress of the work which raises one to a high emotional pitch, a rare feeling of happiness; his spiritual exaltation stimulates his physical power, and causes the investigator-discoverer to forget all the usual necessities of the body. This joyful feeling has been experienced by everyone after he has recognized or made certain of a new scientific truth as the result of experiment. It is not the momentary practical value that calls forth the feeling of happiness, but the knowledge that the great Creator and Ruler of the Universe has revealed to us something which has heretofore been hidden.

One often hears the question: Has this or that scientific observation or discovery any value or use? The history of the development of science and culture has invariably shown that value or use are only relative terms, and are in only partial dependence upon time, place and culture. The answer which the great Benjamin Franklin once gave still holds good to-day. One asked concerning the value of discovery. His answer, as you know was: "What is the use of a child? It may become a man!"

Thus far I have depicted experiment as the basis for chemical knowledge and advances in chemistry. It is indeed an enlightening fact, perhaps especially so at present, to note how in the olden times words of caution were continually expressed condemning the metaphysical and philosophical method in chemistry.

Even Geber about the year 1200 deemed it necessary to advise warningly: "The beginner in science should not despair. If he is looking for knowledge he will find it, however not by the study of books but by investigation of nature."[1] Not the study of the works of the Greek and Alexandrian philosophers and pseudo-alchemists, but a direct experimental study of nature itself.

We are strangely moved to find again in the year 1600 Crollius differentiates between two types of chemistry and speaks with words of warning: "Alchemy is of two kinds, namely, the natural, greatly honored by the children of the arts, and, on the other hand, the sophistica or false, greatly despised by these. . . . Consequently, in this subject no one should believe more than that which experience teaches."

Hundreds of years sank away in the sea of eternity. Then did the great Berzelius say at the beginning of the nineteenth century, "Chemistry is 99 per cent manual labor and practice (that is, an art attained by work) and only 1 per cent theory." Despite this statement, Justus Liebig, then a student, was obliged to listen to a chemical natural philosophy rather than chemistry. About 1840, Liebig criticized this metaphysical era in natural sciences and chemistry in the statement: "The activity and influence of the natural philosophers up to this time was the pestilence, the black death of the century," and especially was this true in chemistry. Does not such a statement as that of the natural philosopher, Carus, to the effect that, "the diamond is a pebble which has come to consciousness," sound somewhat strange to our ears? It was the opinion of K. W. G. Kastner (1806) "that iron in combination with hydrogen goes over to carbon," or conversely that "carbon appears as iron upon loss of all hydrogen."

To-day we should regard these chemical definitions as absurd. That these were even acceptable one hundred years ago gives us food for thought, particularly if we

[1] Geber, *Summa perfectionis*, Chap. 100.

examine with a critical eye some of our own modern views. For scientific fads and errors recur periodically in the development of the science.

The very fact that leading investigators and naturalists had found it necessary to issue warnings from time to time demonstrates that recurrent ascendency of the metaphysical line of thought. We can, therefore, understand why, toward the end of the nineteenth century, a certain Hermann von Helmholtz recommended to those pursuing the natural sciences "the strict discipline of the inductive method, a faithful adherence to the facts which made the natural sciences great"; why he praised those who were attempting to "remove from the natural sciences all metaphysical frauds and arbitrary hypotheses, and were striving to make them the increasingly pure and truthful expression of the laws governing the facts."

III. AIMS AND PROBLEMS OF THE OLD CHEMISTRY.

In medieval times one spoke of chemistry as a "divine" or wonderful *art*. Divine "because the works of God are of two kinds: The work or course of nature comprises Philosophia; the works and ways of Christ, Theology. In the practice of both of these should all mortals spend their earthly existence."[1] Paracelsus taught that "Alchemy is the completion of all nature—and that the stomach is the true alchemist," and that "medicine rested on four pillars, Philosophia, Alchymia, Astronomia and Physica." Without these one could not begin the work of "preparation, separation and true analysis" or "the solution of natural things." One sees therefore that a great philosophical *art*, a wide and diversified *knowledge* including all of nature, and a thorough practical *ability* which must be acquired by constant practice, are required.

How and for what purpose shall this divine art be used? Crollius gives the following answer: "With heartfelt invocation of God and thankful soul this art is to be used

[1] Crollius, *Basilica Chymica*, p. 71 (1629).

for the glory and praise of their Creator, for the benefit of their needy fellowmen, and for the honor of this art, Amen."

We can learn much from this three-century old characterization of chemistry. The purposes and activities of chemistry were not in those days limited to mere technical knowledge. Chemistry was altogether a study and knowledge of nature; its application was service to mankind, in the name and to the glory of God, as the Creator and guide of nature and of the world. The old chemists were imbued with the idea of a kind of divine service or *idyllic* research, and a feeling of union with God.

I made the remark just now that an idealistic searching imbued the old chemists. Many fundamental writings were credited to the old monk Basilius Valentinus. Is it not remarkable and characteristic of the sixteenth century and its people, that this monk never lived and consequently did not himself write these volumes, but that the actual learned author has hidden his identity under this pseudonym?

Does it not make us modern chemists and narrow specialists somewhat retrospective when these, so often misunderstood and ridiculed chemists, so-called alchemists and iatro-chemists, are depicted as veritable romanticists, idealists and moralists. Should we not glean some teachings for our own spiritual guidance from these long past times? Has it not unfortunately become a fact that in our research we have practically lost all touch with nature: that our chemistry is no longer a "natural science"; that it no longer represents a knowledge of nature as a whole, but that it threatens to resolve itself into a host of individual sciences?

Even to-day, looking back but a few years, we can hardly conceive how Joseph Black (1728-1799) could be at the same time a physician, a physicist and a great chemist; or how the romanticist of science, Joseph Priestly (1733-1804) could be a theologian, a linguist, a physicist and a chemical discoverer *par excellence;* or how Jacob Berzelius (1779-1848), physician, could at the same time be a pioneer

in mineralogy and a world leader in chemistry; how he could master the applied, analytical, physiological, inorganic, organic and theoretical branches of chemistry in classical style, and how he could unify inanimate and living nature by their chemical relationships and processes. . . . Is it not true that we have become rich, yes very rich, in details, but poorer in "natural science"? Have we not cause for serious concern over the future development of a chemistry, so productive in individual facts, but so unsatisfactory from the point of view of the great ideas in a world of inanimate and living matter?

IV. BIOCHEMICAL AIMS OF THE OLD CHEMISTS

> Chemistry is the imitator and rival of nature. Its field is almost as wide as that of nature itself; its relation to physics is as that of poetry to the other forms of literature.—*Diderot.*

This proud and frequently quoted passage originated amongst the French encyclopedists at the time when the mechanistic view of life in De la Mettrie's "L'homme machine" and in Holbach's "Système de la Nature" (1770) found its expression.

However, Chemistry was shown this goal many centuries before! Let me quote several passages from an old book.[1]

In order to imitate natural processes "Time, mass and weight . . . are necessary." The alchemists say that they "reverse the orderly processes of nature with their highly developed art, and that they can revert all matter to the *materia prima*." They, the goldmakers, boasted still further "that they, by their art, excel nature, for not only can they restore to life things which have died, but they can also give life and soul to the inanimate, something which nature had not done either because she was not able or did not wish to do so." Again they claim that "human beings and other living animals can be created in the laboratory with flesh, bone and senses, and can be given a soul," and

[1] Biringuccio, *Pirotechnia*. Vannoccio Biringuccio (1480-1538) was a famous builder and metal worker of his time in Rome and Florence. His book "Pirotechnia" is a classical text-book of industrial chemistry. It appeared in Venice in 1540 and recently has been translated by Dr. O. Johannsen (Vieweg and Son, Braunschweig, 1925).

that they "can generate trees and plants without their natural seeds," that "burned or carbonized wood as well as metallic ashes, which have gone through the smelting fire, can be made to grow, foliate and bear fruit." This "divine and supernatural art can create power and riches at will. It restores health to the sickly." Concerning those who have reached the senile age, "it transforms the old man into a youth, stronger and more handsome than he originally was." Finally, "those who have almost passed into the Beyond can, by its power, again regain the strength to live". The preparation in question is called by the alchemists sometimes "quintessence," again "Philosopher's stone," or "potable gold."

Biringuccio thus portrayed the supreme aim of chemistry or alchemy. At what time was the omnipotence of chemistry so heralded? When did this earlier "Age of Chemistry" exist? In the year 1540! Even then the fundamental premises of chemical work were:—time, mass and weight, as well as reversibility of chemical reactions. How similar are the ideals of the past and our present! The *generatio aequivoca* or spontaneous generation, the palingenesis or the regeneration of dead matter, the question of Homunculus and the rejuvenation of mankind, etc., are these not problems of our own times?

Does not Biringuccio speak truly concerning these problems of the alchemists when he says, "If the claims were really justified, they should not have given their art the name, alchemy, which it now bears, for they could have said that they have God, the Creator of all things, locked in a flask?"

May I now be permitted to make an excursion into the field of modern medicinal remedies? You all know the meaning of sunlight therapy. You also know the part played in medicine by mineral salts as foods, and as blood and nerve tonics. You have surely heard of the recent curative methods involving the use of acids (acid therapy) some inorganic, others organic. Diseases of the respiratory system, etc., are cured by them. But even dermatology, neurology, ophthalmology, etc., employ substances of this

sort. All of these are important problems of modern medicinal science. But why do I mention these things here? Simply to show that for such cases the old chemists, alchemists and iatro-chemists could well be our teachers, were we to study the past of chemistry more thoroughly. Consider the times three centuries ago. It is a proud maxim which held sway at that time

"In sale et sole existunt omnia."
(Life depends on salts and sunshine.)

Oswald Crollius,[1] in Wittenberg, recognized as the most influential disciple of Paracelsus, writes in his book "*Basilica Chymica*" (Frankfurt, 1629):

"Not without cause do the ancients say that everything is contained in the sun and in salt." He also states that special powers were ascribed to those acids obtained from sodium chloride or other salts by distillation with clay. Among these were spiritus salis (hydrochloric acid), spiritus salis nitri (red nitric acid containing oxides of nitrogen). On the basis of the experience of Paracelsus, Crollius recommends[2] the spiritus salis for about twenty diseases both internal and external. Rudolf Glauber, known as an industrial chemist, greatly extended (1650) the list, requiring some five folio pages to enumerate all the diseases for which hydrochloric acid in various doses acted as a curative. That was three centuries ago. To-day we state it in another manner and say that the hydrogen ions are vital. "All living nature is regulated by the hydrogen ion concentration. Health and sickness, life and death, are ruled by it," says Arrhenius.[3]

V. THE TRANSMUTATION OF METALS

Even though Geber,[4] in the 12th and 13th centuries, describes and praises the refinement of metals, he differentiates between *imperfection* and *perfection*. The way to go

[1] Oswald Crollius (died 1609) was an outstanding physican (iatro-chemist) who knew what fulminating gold was. He introduced the preparation and the terminology "horn-silver" (luna cornea) for silver chloride, and first prepared tartarus vitriolatus, potassium sulphate, from potassium carbonate and sulphuric acid.

[2] Op. cit., p. 145 ff.

[3] Arrhenius, *Die Chemie und das moderne Leben*, p. 280 (Leipzig, 1922).

[4] *Liber de investigatione perfectionis*, 280 (Leipzig, 1922).

from the first to the second is the "praeparatio." He says "Preparation involves the removal of the superfluous, and the addition of whatever is lacking to bring perfection to an imperfect body.". . . "This can only be accomplished by application of specially adapted methods and the use of purifying agents." . . . "Experience has guided us to various working processes, such as calcination, sublimation, descension, solution, distillation, coagulation and fixation." The substances which have been found to be useful in this preparative work include "all sorts of salts, alums, vitriols, as well as glass, borax and related substances, very sharp vinegar and fire." These are the experimental bases of alchemy. Are these not also the principles which we have contributed to the origin and development of our present-day chemical knowledge? Are not the old working methods of seven hundred years ago still employed to-day? And is not the purpose of these operations, these preparative methods, namely, that of the purification of materials, scientifically *correct*? Are not both Analysis and Synthesis represented in this ancient methodology? Are we then not heirs, imitators and developers of these past ages?

We have too often ridiculed and misunderstood the alchemists. Justus von Liebig[1] was right when he said, "Alchemy has never been anything else than chemistry. It has been done a great injustice by confusing it so constantly with the gold-making arts of the 16th and 17th centuries. Alchemy was *a science*, and it included also all branches of the technical-chemical industry."

Besides the old rules for the refining of metals by purification, which I have just given, the important chapter on the *transformation of metals* is still intact in the old chemistry. Let me point out incidentally that the theoretical or metaphysical basis for the "possibility" of such a transmutation is founded in Aristotle's philosophy, namely, in the original substance, *prima materia*. We are, however, primarily interested in another side of this

[1] Von Liebig, *Chemische Briefe*, 3te Brief (1850).

subject "transmutation." Were there any facts which would have led then in olden times to conclude that in chemical operations with the metals lead, copper, mercury, silver and gold, such a transformation had taken place? Or, to put it differently, was it not necessary to assume from certain very definite facts that a complete transformation of most metals into gold had taken place, when one consider the then status of the chemical methods for separation and purification?

Again, did the experienced metallurgists and practical chemists of that day really believe in transmutation? The latter question is truly important, the more so, since it has usually been disregarded altogether in passing judgment on the idea of transmutation.

Let me answer immediately and in the *negative*. The real authorities on metallurgical chemistry gave no credence to the possibility of artificial preparation of gold. Two practical chemists may be quoted as witnesses. One is Biringuccio. In his classical work "Pirotechnia," written at the beginning of the 16th century, he not only disavows all possibility of artificial preparation of gold, but he adds, "I would have to regard people as very clever, a sort of terrestrial angels, were I to believe that they could accomplish this."[1] Even though the other witness, the outstanding practitioner Rudolf Glauber, defended the transmutation idea, he nevertheless writes: "I will not seek to prove, nor could I do so, that he (Paracelsus) could make gold and silver in large quantities. . . . but only stated that it is possible to do so, and this is all I undertook to prove. How to do so on a large scale I do not know at present, nor am I particularly interested to know."[2] From this indirect statement we can plainly see that to him transmutation was regarded as *hypothetically* possible, but that practically he had never actually accomplished it and did not regard it as important. For he says in evident disdain of his theoretical proofs, "nor am I particularly interested to know."

[1] Op. cit., p. 36 ff.
[2] Glauber, *Opera Chymica*, I, p. 369 (1658).

But to return to the other question. Were there any reasons which, to a slight degree at least, made it necessary to assume that a transformation to gold had taken place? This question can be answered in the affirmative. We may count among such facts the finding of *smaller* or *larger traces* of gold during the course of the ordinary metallurgical processes, a fact which was emphasized again and again. Even the great alchemistical scientist, Albertus Magnus (1193-1280) teaches that gold is found in all minerals. Three hundred years later Biringuccio, whom we have already quoted, writes: "there are few metals which do not contain a trace of gold, some more, some less." Glauber even suggests the *reagents themselves* as a source of gold in chemical processes. He obtained gold as a residue after he had dissolved fine silver in aqua fortis, precipitated it with salt water, washed, melted and reduced it to silver, remelted it and then dissolved it again in aqua fortis. Then he inquires, "Where did this gold come from? From the silver, the aqua fortis, or the salt water, the three substances which were used in the reaction?" It was his belief "that the spiritus nitri had carried over some gold which was present in the iron or copper vitriol used in the distillation."[1] Is not the negative attitude with reference to the sudden appearance of gold in pure silver a remarkable thing about this argument? What could be more logical than for Glauber to assume that a transmutation had taken place, that is, that gold had come into existence? Glauber regards this question or the "possibility" as so improbable that he does not even mention it, but proceeds in a critical experimental way to examine the reagents used in solution and precipitation to ascertain whether they contained gold. The crude nitric acid, prepared by the distillation of saltpeter and vitriol, he regarded as the probable source of the traces of gold found later in the silver, the particles of gold being carried over from the vitriol during the process of distillation.

Two things can be learned from that which has just been presented: first, that the occurrence of small traces of

[1] *Opera Chymica*, I, p. 112 (1658).

gold in minerals was recognized many hundreds of years ago; secondly, that the elimination and separation of these minute quantities of gold is accomplished with great difficulty, so that gold that was found in the product of a chemical reaction might be mistakenly thought to have been formed in the process. Glauber's insight must be regarded as truly remarkable, and his statement shows that the clever investigators of long ago knew that the gold was not created in the experiment.

Even if these men, learned in their art and in the knowledge of minerals, did not regard the sudden appearance of traces of gold as transmutation, and did not ascribe its origin to other metals, but traced back its source in classical nineteenth century style to minute quantities present in the reagents or apparatus, the theorists were of an altogether different opinion. Their greatest authority, Aristotle, held that metals were formed from the "original substance" and believed in the growth of metals in the earth and from vapors. The alchemists therefore argued that gold could come into existence during chemical processes. For, they added, did not one actually find it in nearly all metals and minerals?

We must admit that we have come to a critical point in our chemical philosophy. Two opposing views are here in conflict. As long as we adhere to the conception of an element and regard its stability as a law, the transmutation idea will have no place in chemistry. Conversely, as soon as this conception of an element begins to totter, the idea of transmutation will gain in strength. It has been so in the past, it is so to-day. Let me speak briefly concerning the present.

What is our attitude and our scientific belief with regard to the transformation of base metals into gold? How long ago was it when, on the basis of our modern theories, the prophecy was made: "If by some agency or other we could only cause mercury to expel an alpha particle (that is, a positively charged helium atom) and a beta particle (a negative electron), the product would be

an isotope of gold."[1] Since then (1913) this statement has been often repeated, unfortunately too often, not only by scientists, but also by the press. As a dogma it has already brought confusion in the minds of the laity, and as a new principle it has served the group of contemporary alchemists and pseudo-chemists to resurrect the old idea of transmutation. Are not statements such as the following often made in popular magazines? "The philosopher's stone has been found!" "The dream of the ancient alchemists has been made a reality by modern science!" As you know, this idea has reacted upon modern science, but certainly not to the benefit of modern exact research. The much-disputed question concerning the transmutation of mercury into gold, which Miethe claims to have accomplished, has involved, since 1924, not only a whole group of chemists, both theoretical and experimental, but also business-like speculators. And what has been the result? Unfortunately the witty chemist is right in saying, "Miethe gold will proably be found to be mythical gold." As before, the old way of making gold (earning money) will be the simpler, less expensive and more dependable.

Soddy's theoretical method gives us a picture of how gold might be formed by the degradation of an element of higher atomic number and greater atomic weight. If mercury, which has an atomic weight of 201, can be robbed of an alpha particle which has a weight of 4, the remaining substance would have a weight of 197 and this is the weight of gold. To-day such a suggestion seems scientific to us. But was not the suggestion Boerhaave brought forward two hundred years ago just as scientific? Silver in his day was represented by the symbol ◡, a corrosive (an acid) by +, gold by ○, and mercury by the symbol ☿. An old English translation runs as follows: "Quicksilver evidently shows gold in the middle or body of it, silver at the top or in the face, and a corrosive at the bottom, accordingly all adepts say of mercury that it is gold at heart, whence its heaviness; that its outside is silver, whence its white colour. . . . And hence that maxim upon

[1] F. Soddy, 1913.

mercury: Strip me of my clothes, and turn me inside out, and all the secrets of the world will come forth."[1] There is much food for thought in these words. Is it not peculiar that, just as to-day, mercury played the rôle of mother substance for the artificial preparation of gold? Does not this old symbol of transmutation greatly resemble the modern one? There "the heaviness at heart," here the atomic mass at the center; there the visible properties ("white color") on the outside, here the outer electrons. Does not the one say "Strip me of my clothes," while the other says "remove an alpha and a beta particle"? And do not the two symbols resemble each other, furthermore, therein that they have remained nothing but symbols, in spite of all experimental efforts? The mode of expression of Boerhaave might well here be used. Not the "clothes" but the "whole skin" would have to be removed!

Let us forget for a few minutes our modern views as scientific aids of a given era. Let us regard as analytical chemists, without any theory, the phenomena accompanying the bombardment of mercury by electrons and the varying traces of gold coming to light during this treatment. Would it not be more logical to assume that mercury, despite all purification, was still contaminated with minute quantities of gold? If the old chemists were able to detect weighable quantities of impurities, such as a grain of gold, by purely chemical means, may not our loading with electrons be the physical aid assisting in the separation of the last traces of gold in mercury, and the isolation of quantities to the order of 10^{-8} to 10^{-9} grams? It seems to me that the difference between the past and present lies, not in the direction but only in the order of magnitude of the applied energy and amount of the impurities which have been separated.

That brings us to the problem of the *purity* of our materials. It is a peculiar and striking characteristic of the older alchemists that they seemed to show no curiosity concerning many substances which they observed in the course of their experiments, and made no attempts to in-

[1] Boerhaave, *New Method of Chemistry* (London, 1727).

vestigate them. Thus we find that these old chemists had seen and described the oxides of nitrogen more than seven hundred years ago, had used chlorine in their aqua regia, had obtained sulphur dioxide directly by burning sulphur in air, knew of the formation of hydrogen from iron and sulphuric acid and of its explosibility—yet all these things had to be "discovered," that is, identified, recognized and differentiated chemically at the end of the eighteenth century!

VI. THE PROBLEM OF "PURE" SUBSTANCES

A Berlin physicist, Peter Riess (died in 1883), known for his work in frictional electricity, is said to have defined chemistry as the "impure part of physics." Let us assume that such was the relationship between chemistry and physics 75 years ago. The question naturally follows, whether the methods or the materials could correctly have been labelled "impure." If we frankly investigate this question, we shall find that his charge is justified. Indeed, the problems of purity and methods of purification are of fundamental importance to both pure and applied chemistry. The gradual progressive expansion of qualitative reactions and methods of separation of the individual metallic and gaseous substances, did not reach its development until the eighteenth century. Particularly well worked out were the wet analytical methods which soon caused the enrichment of chemistry by 15 new elements. Further differentiation of substances hitherto regarded as homogeneous, by electrochemical and spectroscopic methods in the nineteenth century, is generally known. Countless substances, now recognized as elemental by every beginner, were then regarded as compounds, and substances later proven to be compounds were considered to be elements. Thus the oxide of uranium for fifty years was thought to be the element, and titanium nitride, TiN, was thought to be the free metal.

According to Davy (1810) the diamond contained oxygen; phosphorus and sulphur were compounds containing these elements together with oxygen and hydrogen. Berzelius defended the opinion that chlorine contained an element "murium." Nitrogen was a compound according

to Davy and even as late as 1825 Berzelius contended that nitrogen was the suboxide of an element "nitricum." The metals potassium and sodium discovered by Davy, were considered by Gay-Lussac and Thénard as compounds of the metal with hydrogen (1808).

If we inquire as to the causes of these erroneous conceptions, the answer is not difficult to find, viz., the undeveloped state of the methods for separation and purification; in other words, the presence of impurities.

If we survey the present, and examine carefully the modern views concerning the nature of the various elements, we find much in common between the newer and the older ideas. The compound nature of the elements was even then a subject for speculation and one which had been repeatedly tested by experiment. The old idea of hydrogen, as a component of all matter, is again accepted in the form of the proton.

Many of our other most modern conceptions find their predecessors in the past. We have already mentioned the fact that Berzelius regarded nitrogen as a compound substance and defended his views very skillfully. That it should be nitrogen which, just one hundred years later, should have been partially broken down by Rutherford's bombardment with alpha rays, is a unique phenomenon in the progressive development of our views.

According to Einstein's theory of relativity, a transformation of mass into energy is possible. It has often been said that such a change, as in the case of one atom of nitrogen, would be accompanied by the evolution of an immense quantity of heat which could become economically valuable. According to the well-known Einstein equation, $E = mc^2$ (where E = energy, m = mass, c = speed of light), a quantity of heat equivalent to that obtained by the combustion of 3,000 tons of coal would be obtained by the destruction of one gram of any substance.

More than one hundred years ago Lichtenberg, professor of physics at the University of Göttingen, made the following statement: "If one could only invent some suitable substance to decompose the nitrogen of the air in

order to set free its heat, it would be one of the greatest discoveries of economic importance." The reversal of the Einstein equation permits the transformation of energy into mass ($m = E/c^2$). The modern successors of the old alchemists, the hyperchemists and theosophists, could well maintain from their point of view that this transformation or materialization of energy has long been known to them. It was reported in all seriousness that in the year 1666, at The Hague, in presence of the physician Helvetius, gold made artificially from lead "actually gained in weight." Another report concerning an incident in Vienna (1716) states that in the transmutation of copper pennies into silver, 125 pounds of silver were obtained from 100 pounds of copper.

Concerning the question of the transformation of energy back into matter we can also quote Glauber from his treatise *De Auro Potabili*, "It is believable that if we knew of a suitable container, we could catch and coagulate in it the rays of the sun as well as the heat from ordinary fire, and thus metals could just as easily be generated on the earth as in the earth."[1] But let us return to our consideration of the historical rôle played in chemistry by "traces" or "impurities." A special volume might be written concerning this influence in the development of chemistry. Think of the part played by catalysts in chemical industry. Consider the vitamins and the most recent experiments of Windaus in physiological chemistry. We will limit ourselves to a few comments.

Material perception and abstract classification follow each other only after long periods of time. Besides the kind of matter, the quantity of matter is important in the history of this development. With advanced analytical-chemical procedure, the smallest traces such as accidental, subordinate and minute quantities of a foreign body become sources for the discovery of new elements. Modern industry has learned to value and accumulate these "traces," and to transform them into appreciable quantities. Take the cases of tungsten, titanium, selenium, thori-

[1] Glauber, *Opera Chymica*, II, 328 (1659).

um, uranium, radium, helium, germanium, etc. At the same time, this change in practical value of what were once impurities has served to develop the method and sensitivity of their detection and recognition. Thus gold can now be detected in quantities as small as 10^{-8}—10^{-9} grams; helium in amounts as small as 10^{-9} cc;[1] one part of mercury in 1 1/2 million parts of coal tar,[2] and iodine in amounts as minute as 10^{-6} gram, can be discovered if present in the soil, plants, meteorites and iron ore, yes, even in steel itself.[3]

We become contemplative when we find, on the other hand, that even in our purest preparations, using the utmost precautions, such "traces" are still detectable. Let us recall the gold from mercury[4] and the formation of helium from tungsten.[5] Let us not forget the discovery that quartz vessels hold gases very tenaciously, even after heating above 1000°C. for many hours and being thoroughly exhausted with a pump.[6] You all know of the remarkable observations of F. Paneth and his co-workers in 1926-1927, which seemed to indicate the transmutation of hydrogen into helium, with the aid of finely divided palladium. More thorough investigation showed, however that the asbestos which was used in the apparatus contained helium. Countless other examples could be cited.

We thus see how barely surmountable experimental difficulties confront us in the case of such simple and stable substances as the elements. The term "purity" can be applied only to an ideal state, in that this condition is approached asymptotically with our experimental technique as it is at present. What then are we to expect in regard to the purity of compounds, of organic and inorganic substances of highly complex nature and by no means stable? How simple—*sit venia verbo*—rather how primitive are still our customary qualitative tests for purity in this field! One could almost say that we of to-day are scarcely

[1] Paneth, 1926.
[2] Kirby, 1927.
[3] Fellenberg and Lunde, 1927.
[4] Miethe.
[5] Wendt and Irion, 1922.
[6] W. Biltz and H. Müller, 1927.

further advanced in the testing of the purity or individuality of complicated compounds, than were the old chemists in the testing of the purity of metals. However, the problem of pure, or we may say "ultra-pure" substances has yet other important phases.

As long as we are satisfied to be able to detect the presence of these previously mentioned "traces" of foreign substances in our purest materials, we stand on the firm ground of experimental analytical chemistry. Berzelius held that chemistry consisted of 99 per cent experiment and one per cent theory. And we have reason to be proud of being able to detect such a small volume of a gas as 10^{-9} cc, which, in simple illustration, would mean that if this laboratory were a single large box full of air, and we liberated a thimbleful of a rare gas in the building and mixed it thoroughly with the air, we could then detect that gas in a sample of air taken anywhere in the building. But in some cases our modern methods of reasoning suggest an "explanation" for the presence of these minute quantities of matter: we say that they have come into existence by transelementation. Is it not peculiar and psychologically interesting that we, with all our logic and weighty experience, should capitulate so quickly to this new idea? In what other branch of chemistry would we so readily accept so radical a theory? Have we not returned to the reasoning and evidence of the alchemists and transmutationists, who believed in transmutation because they wished it?

We are witnesses to-day of a tendency in research against which we were warned long ago. It was Crollius (1629) who, three centuries ago, pointed out the danger of the "*Sophistica*" or false chemical art. Helmholtz earnestly recommended thirty years ago a cleansing of the natural sciences of all metaphysical, fraudulent deductions. The scientific cult of minutest quantities is in fact just as characteristic of the present day as is our development of large-scale processes in the industries. If we consider the lessons of the past, and take as our guide the natural causes for the occurrence of these minute quantities, are we

not justified in asking this question: Has the so-called destruction of the atom into unweighable quantities of protons and traces of helium, with total exclusion of impurities from the materials and the apparatus, been realized and can it be realized?

In addition to these metaphysical deductions and theoretical conclusions, whose greatest importance is inversely proportional to the smallest traces, there are other questions for the experimental chemist. For example—What are the chemical properties of the "ultra-pure" elements and compounds? In what physical state and in what chemical combination do traces of substances exist, such as gold in mercury, iodine in steel, gas on the surface of quartz? So we pass from the past with its teachings to the future when we say—In addition to our present chemistry, a future "chemistry of 'ultra-pure' substances" must arise; not only the physical condition but also the reactions of these "ultra-pure" substances must be investigated. How do these substances react on one another? How do they behave in great dilution? Is it not peculiar that matter in the "ultra-pure" state behaves very much like the so-called "unsaturated compounds", as is shown by the behavior of ultra-pure water, the Baker extremely dry bodies, and the like?

We have come to the end of our discussion. Can we and should we learn something from the old chemistry, from its masters, its methodology and its aims? I think the answer is "Yes!" A peculiar rhythm controls the development of chemistry. People and times change, yet certain ideas and ideals persist. True enough they undergo a change in form and value with the course of time, but they live on from generation to generation and act as guides for chemical reasoning and research.

Pascal's words will ever remain true: "La suite des hommes pendant le cours de tant des siècles doit être considéré comme un même homme qui subsiste toujours et qui apprend continuellement." (The succession of men during the course of many centuries should be considered as one and the same man who exists always and learns continuously.)

PART I
SALTS, ACIDS AND BASES

CHAPTER I

Historical Development of the Concepts

THE history of our knowledge of acids, bases, and salts, is a large and important chapter in the history of chemistry. If metals represent the one pole of chemistry, then salts form the other pole for theory and practice. This history is important not alone for the chemist—it also plays an important part in the history of the world and civilization. Think of the part played by common salt and saltpeter in economic questions that involved both the political and social rearrangements of nations. Think of the part played by nitric, sulphuric and hydrochloric acids in the development of chemical technology, in the preparation of new salts, their application in the dye industry, medicine. Think of the alkalies, potash, natural soda, caustic potash, in the glass and ceramic industries, manufacture of soaps. The history of the gradual growth of our knowledge of salts, acids, and bases is furthermore an interesting chapter in our intellectual history, for it concerns a complex problem whose chronological development we may follow without a gap for seven hundred years. To-day the answer to the question: "What is salt?" seems to be simple. How peculiar indeed is the line of development of this thought concerning the nature of salt! Variability on the one hand, inflexibility on the other, variety in kinds and types of salts as opposed to a primary, or proto-salt, as the resting pole. Unity or dualism and polarity! First, everything that is soluble in water is called a salt, then acids and bases are differentiated from salts. Acids are at first called spirits, "spiritus," then they are materialized and finally are regarded as oxygen compounds or as substances which contain a hydrogen atom replaceable by metals.

We shall attempt to discuss the question Salt-Acid-Base in three ways: first, from the standpoint of abstract historical development, on the basis of purely chemical work; second, with reference to their behavior towards electricity, as electrolytes and non-electrolytes; and third, in relation to the nature of the solvent in particular non-aqueous solvents and their electrical conductivity.

Our discussions will therefore divide themselves into three parts.

1. "SALT" IN THE CHEMISTRY OF GEBER (ABOUT 1200)

The prototype of all salts, the basis for their terminology and the views concerning them through several centuries, is "salt," sal gemmae, or sodium chloride. Following this closely come sal ammoniacum or armoniacum, sal ammoniac, ammonium chloride; then sal petrae or petrosum, or salonitron, sal nitrum, saltpeter or potassium nitrate; also sal alkali verum from alkali plants, K_2CO_3 and Na_2CO_3, or sal alkali obtained from ashes, consequently impure potassium hydroxide. Finally an organic salt "tartarus," acid potassium tartrate or crystallized Weinstein, sal tartari or calcined residue of distilled wine (mostly potassium carbonate); oleum tartari which meant sal tartari that had become liquid in air.

A group of five different salts given the descriptive term "sal" represents all the salts known to the alchemistry of Geber in the 12th and 13th century. It may be noted that the same name did not always represent the same salt and the same composition. For instance 'sal petrae' was often used for rock salt; 'sal nitrum' often referred to soda. Geber does say "Various other kinds of salts have been discovered,"[1] but a detailed consideration and discussion is lacking. He differentiates between "salts, alums, saltpeter, borax." He says "those substances must also be studied which purify metals, without combining with them. These are salt, alums, saltpeter, borax and related substances." Later he states that "substances with which

[1] Darmstädter, *The Alchemistry of Geber*, p. 98 (1922).

preparation may be carried out, include all sorts of salts, alums, vitriols as well as glass, borax[1] and related substances, very sharp vinegar and fire."

What a salt really is, what characteristics salts possess so as not to be grouped for instance with the vitriols, were not specified. One property does differentiate them from metallic ashes and metals. To quote, "Salts can easily be separated from the sublimation residue by dissolving them. This is not possible in the case of other substances." We probably approach the conception of that period when we define a salt on the basis of its physical characteristics, not chemical composition or reactions as follows:—A salt is a substance which is soluble in water from which it can be separated in crystalline state, and from which it can be obtained as a residue on heating. Geber himself says: "Everything which is to be dissolved must be of the nature of a salt, alum, or a similar substance. These substances have the property of melting before they turn into a glass-like mass"—that is they melt in their own water of crystallization which they subsequently lose. The ancients had no conception of the "nature," the chemical composition, of these salts, but considered rather their physical behavior and uses. Sulphur is described as follows: "By the highest God, sulphur improves every substance for it is an alum and a tincture."

In the years that followed the meaning of "salt" is expanded and differentiated more and more. We step from the limited field of the alchemistical practice to metallurgy and chemical technology, beginning with the 13th century. Saltpeter is used in the manufacture of gunpowder, for the preparation of aqua dissolutiva (aqua fortis, strong water, our nitric acid) together with vitriol and alum. Vitriols are employed for the preparation of oil of vitriol, and together with salt to make Salzgeist, hydrochloric acid. Vitriols, alums and sal ammoniac were also used to some extent in dying, painting, brewing, and otherwise.[2]

[1] Borax is given the name "sal borak" in the *Bergbüchlein* at the beginning of the 16th century. See Darmstädter, *Berg-, Probier-, und Kunstbüchlein*, p. 38, 41 (Munich, 1926).

[2] According to Biringuccio (1540) alum was used in the "dyeing of cloth and wool, in which processes it is as necessary as our daily bread."

II. SALT IN IATRO-CHEMISTRY

"In sale et sole existunt omnia"

Sixteenth Century

At the beginning of the 16th century new views concerning salts arose, the change being largely due to the theoretical classification of all nature by Paracelsus. He taught that man and the world are one and the same, and said—"There are three things which are present in every body. That is every body contains three substances. The names of these three substances are sulphur, mercurius and sal."[1] These can be shown in the case of wood: "It is a body, let it burn. That which burns is sulphur; nothing burns except sulphur. . . . That which smokes is mercurius; nothing sublimes except mercurius. That which goes to ashes is sal; nothing becomes ashes except it contains sal. Take a human being: his body is nothing but sulphur, mercurius, and sal. In these three things are contained health, sickness, and everything which pertains to him." It is the unity of composition of matter of all nature which Paracelsus first proclaims. All things so far as they are corporeal, consist of the trinity sulphur-mercurius-sal. "It should be mentioned beforehand that man, like the metals, arises from sulphur, mercurius and sal."[2]

Furthermore, the principle of equilibrium or unity of this trinity is emphasized. "Dissension" among the three "substances" is the beginning of all diseases, "for as soon as the three are united and not separated, health follows."

The part played by the substance "sal" can be gleaned from this statement: "Sal gives color and form to all creatures."[3] "Sal is that which keeps a body together."[4] "Even if they have come together to form a body, there are only three substances. Sulphur burns for it is only sulphur. Salt is converted into an alkali for it is fixed substance. Mercurius is a smoke, since it does not burn but leaves the fire."[5] Salt (sal) therefore imparts to a body

[1] Paracelsus, *Opus Paramirum*, I, p. 72 (Huser's Edit.)
[2] Idem, *Manuale*, IV (Huser's Edit.)
[3] Idem, *De Pestillitate*, III (Huser's Edit.)
[4] Idem, *Vom Bad Pfäffers*, VII (Huser's Edit.).
[5] Idem, *Opus Paramirum*, I (Huser's Edit.).

the property of resisting fire, gives the body form, and conserves it. Paracelsus differentiates between three types of natural salts: sal, vitriolum, and alums.[1]

In Geber's times salts played a somewhat subordinate rôle, in that they were considered merely as materials (corrosives) in the alchemistical attempts at transmutation or purification. They were substances which "were useful in the process of preparation,"[2] where they served as "medicines" for the purification of "imperfect" metals. Paracelsus, however, placed them at the center of his naturalistic system. For the intellectual world, "sal" became one of the three fundamental "elements". The lesson of sal, sulphur, and mercurius, was such that it pointed the way for the further development of theoretical views in chemistry. "Salt" as the representative of a definite class of substances became an important material problem in chemistry. The "salt" as a fundamental drug served to keep medicine supplied with new problems for some centuries. Medical men soon took over the preparation, chemical investigation, and determination of the therapeutic value, of the new "salts". In addition to the principle of the unity of matter in minerals, plants and animals, there arose also the principle of the similarity of chemical reactions in animate and inanimate nature. "The stomach is the alchemist," says Paracelsus, "and the alchemist in man should serve as an example to the practical alchemists."

There is no doubt that the chemical practicians of that time attempted to approach the problem of the nature of salts from the material side as well. The following example quotes an opinion of Biringuccio, who writes (1540) concerning the nature of vitriol in his "Pirotechnia":[3] "It is my opinion that there are five different qualities in vitriol, namely, the property of sulphur, the appearance of alum, the biting effect of saltpeter or of salt, and, of the metals, the properties of iron and copper."

It is indeed of interest and value to us to examine this description of vitriol dating from the year 1540. It is not

[1] Idem, *Von den Bergkrankheiten*, Book II, 3d tractate.
[2] Geber, *De Investigatione Perfectionis*, Cap. IV.
[3] Ibid., Book II, Chapter V.

individual substances which are sought, but analogies in quality. One did not say that vitriol *contains* sulphur, but that it *shows* the quality of sulphur—corrosive vapors are emitted both when sulphur is burned and when vitriol is heated. One did not then say that vitriol is composed of copper or of iron, but rather: vitriol contains the properties of iron or copper. The old form of expression was actually the most pertinent, for it related directly to the observed properties of the substances. It was entirely satisfactory because the number of observed properties was at that time too limited to warrant decision as to complete identity.

Period 1650–1700

In the early days every new *compound* body represented a new riddle. The old alchemists sought to resolve such riddles, in a certain measure, by the same mental and experimental operations as we modern chemists employ with regard to the new and old chemical *elements*. In general we can proceed from two standpoints: (1) from the external consideration of the new object, from the form, size, etc., and by comparison with well-known mechanistic models and actions reach a conclusion from these sensual, visible, and perceptible properties, as to the invisible, hidden nature of the bodies; or (2) we start from the given chemical components of the object and seek the connection between these supposed internal components and the observed external properties. The first way is a mechanistic procedure, the second, analytical and synthetical, is a chemical way. We shall see that both of these methods were used and both gave a lasting impulse to the coming investigations of "salts-acids-bases".

Form as the Cause of Differences.—Robert Boyle (1626-1691) wrote in his book, the "Sceptical Chemist" (1661): "It seems not absurd to conceive that at the first production of mixed bodies, the universal matter was actually divided into little particles of several sizes and shapes variously moved." Quoting from his paper "Of the Usefulness of

Natural Philosophy'':[1] ''The operations of dissolvents are so determined by various textures of bodies, on which they are employed. . . .'' He says in his tractate ''Of the Producibleness of Chymical Principles'' (Part IV): ''for dissolution depends not so much upon the pretended cognation between the solvent and the body it is to work on, as upon the congruity, as to size and figure, between the pores of the latter and the corpuscles of the former''.

Form, size, and movement of particles are represented as the deciding factors in chemical reactions. The latter include also solution by acids. There are no hypothetical kindred forces or ''affinities'' which lie hidden in the individual kinds of matter that bring about reaction with other substances, but actual, mechanistic causes, which are to be regarded as characteristic. Forms of bodies, pores, etc., of the sensual, visible substances of the external world lead to conclusions with reference to the deductively inferred, hypothetically constructed particles or corpuscles of matter. From matter in the mass one deduced the properties of the smallest ultimate particles. Chemical properties are not determined chiefly by difference in material components or material composition, but rather by the forms which the bodies show. Even Aristotle regards form (eidos) in contrast with matter (hyle), as the intrinsic property of a substance. The ὕλη is the original substance, πρώτη ὕλη = materia prima, the homogeneous substratum (basis) of all changes, and the ''abstract assumption'' as to the possibility of a material world—is predicted upon the assumption that the actual formation of individual substances occurs only when they take a definite ''form''. If we ascribe a definite form to each of the substances which we call acid, base or salt, should there not be a primal or proto-acid, a universal or proto-salt, and a primal alkali? This assumption seems entirely logical if we accept the premise of the unity of matter of the whole material world. We shall see that this conclusion was also drawn at that time.

[1] Part II, Section I, published in 1663.

Let us now turn to Nicolas Lemery (1645-1715) who was the chief promoter and champion of the corpuscular theory in chemistry. He wrote as follows in his "Cours de Chymie":[1] ". . . personne ne peut douter qu'il n'y ait dans l'air un Acide capable . . . de penetrer les pierres et les terres, puisqu'on remarque tous les jours que les terres . . . en reprennent de nouveau et augmentent de poids considerablement . . ."

If we examine these statements in the light of our present day theories, it is not difficult to detect a certain amount of agreement between them. Is not the "acide" of the air which permeates all minerals and ores and causes them to increase in weight, and which occurs also in saltpeter, the same thing as Lavoisier's oxygen? Does not Lemery in 1675, therefore, prophesy and prepare the way for the "oxygen theory" of Lavoisier (about 1775)? At least we will have to admit that both Lemery and Lavoisier regarded the acid principle, (Lavoisier's oxygen), as existing in the atmosphere. However, Lemery is a forerunner of the modern age in other respects.

How are acids, bases, and salts defined by Lemery? Upon what facts do their differences rest? "Comme on ne peut pas mieux expliquer la nature d'une aussi cachée qu'est celle d'un *sel*, qu'en admettant aux parties qui le composent des figures qui repondent à tous les effets qu'il produit; je diray que l'acidité d'une liqueur consiste dans les particules de sels pointuës lesquelles sont en agitation." One can see from this quotation that the term salt, "sel", as a generic name includes also the acids, and supposes the form of particles to be the characteristic property. Further, Lemery supposes the existence of a primal or universal salt.

An *acid* is a substance "composé de parties pointuës lesquelles sont en agitation." This supposition is justified not only by its action on the tongue, but also by the crystal form of the acid salt—"ces crystaux sont composez de pointes différentes en longeur et en grosseur les unes des autres, et il faut attribuer cette diversité aux pointes plus ou moins aiguës des différentes sortes d'acide."

[1] First Edition, (1675); Fifth Edition, 15 (1683).

Conversely an *alkali* is "une matière composée de parties roides et cassantes dont les pores sont figurez de façon que, les pointes acides y estant entrées, elles brisent et écartent tout ce qui s'oppose à leur mouvement."

We can see that Boyle and Lemery (about 1675) ascribe the variety in the material world not so much to the differences in the material nature, but rather to differences in form and size of the particles of the various substances. Space and stereochemical factors help or hinder chemical metathesis, and are responsible for the stability of chemical compounds.

There were times when one ridiculed these crude models. If we modern chemists, after two hundred and fifty years of chemical development, critically examine these methods of reasoning of long ago, we not only shall judge them less harshly, but find many points of contact and relationship with our own views. We regard with wonderment the accomplishment of Rutherford who in 1919 brought about the "disintegration of the nucleus [of the nitrogen atom] by bombardment with swift alpha particles", positively charged helium atoms forcing their way into the *nucleus* of the nitrogen atom. We talk of "*shells* of electrons" and of their "deformation", of the "linking" of two adjacent atoms, of the "attachment and incorporation of two molecules," of "the lattices of ions and molecules." We allow molecules to "interlock" or to "penetrate" one another.[1] Are these not mechanistic portrayals like those of past times?

Let us summarize the views in the time of Lemery in 1675.[2] In general we must say that Lemery does not consider the material nature of individual salts, alkalies, and acids, but that all acids or salts are based on a general principle and can be differentiated by spacial properties. Consequently he assumes the existence of a primary type of acid, a universal acid, and a universal alkali, from which a universal or primal salt may be formed. Only

[1] Koppel, Z. Elektrochem., 26, 319 (1920).

[2] Lemery's famous *Cours de Chymie* was re-edited up to the year 1756; therefore his ideas were in circulation and influenced the mechanistic views in the second half of the 18th century.

differences in the geometrical form (configuration) and appearance of the particles are involved in the differentiation of the various kinds of salts, acids, and alkalies.

One should not forget to mention John Kunckel, the great practician, who voiced his opinions against the mechanistic explanations with the aid of points, thorns, pores, screws, clasps, etc. of the particles.[1]

No advance in the chemical knowledge concerning the nature of salts was made by the leading English chemist of that period, Robert Boyle when he wrote "It [a salt] is easily dissoluble in water and it affects the palate with a savour, whether good or evil."[2]

This definition includes a property which Geber had already ascribed to salts, namely, their solubility in water. The second distinctive property has to do with their effect upon the taste nerves, a characteristic derived from iatrochemical practices.

Acids were characterized by Boyle as follows:

1. They dissolve many substances;
2. They precipitate sulphur from its solution in alkalies;
3. They change blue plant dyes to red;
4. They lose all these properties on contact with alkalies.

Conversely, alkalies lose all their properties on contact with acids. The reaction usually takes place with effervescence.

Substance as the Cause of Differences.—While the believers in the corpuscular theory regarded the form of the corpuscles as the deciding factor in the material world and in the chemical nature of salts, another group of chemical investigators and thinkers were at work determining the material differences in the various compound substances. Chemical analysis and synthesis came into use. The principle of the conservation of weight, as well as that of the conservation of chemical type, were gradually applied, even if only in a few scattered cases. The salt was divided in-

[1] Kunckel, *Laboratorium Chymicum*, p. 135 (1722).
[2] Boyle, *Experiments and Notes about the Producibleness of Chemical Principles*, p. 3 (1680).

to two components which represented chemical (but not geometrical) opposites. Upon this development J. H. van Helmont, Tachenius, and particularly Rudolph Glauber exercised an enduring influence.

Joh. Bapt. van Helmont (1577-1644) says of salt, that even in solution it retains its identity. "Just as salt, after it has been dissolved in water can again be made into salt without change. . . ."[1] In speaking of a solution of potassium silicate he says that free silicious earth is precipitated out on the addition of a sufficient quantity of aqua fortis "quae saturando alcali sufficit."[2] The term "saturare", saturate, here is met for the first time. It appears as though the word "saturare," as well as "saturation" which came into use later on, are copied from the observed phenomena in the organized body, much as the following descriptions of chemical reactions are imitative of the animistic conceptions. He writes: "Nothing is devoured by it"—speaking of a glowing coal in a closed space. "All matter must revert to its original state. Accordingly all the incidents of its creation which have infected it, must first be taken from it by killing and extermination of cold."

Likewise prominence must be given to the activity about the middle of the 17th century of a Westphalian druggist and physician, Otto Tachenius (Tacken). In his work "Hippocrates chemicus" (Venice 1666), he says that all salts can be broken up into two components, an alkali and an acid: "Omnia salsa in duas dividuntur, in alcali nimirum et acidum." However, he regarded alkali and acid as primal substances of all nature and considered them the components of all substances.[3] Opposed to the very exactly phrased definition of "salt" by Tachenius, which is so similiar to our present-day conception, is the less satisfactory view of his contemporary, John Mayow (1643-1679). Concerning his memorable investigation on saltpeter (1674) he says "If the disintegration of saltpeter by distillation is carried out, an acid "spiritus" will

[1] Fr. Strunz, *J. B. van Helmont*, p. 28 f.
[2] *Ortus Medicinae*, p. 56 (1648).
[3] Tachenius, *De Morborum Principe*, Cap. II (Bremen, 1668).

collect in the receiver, while fixed saltpeter, which is very similar to alkali, remains in the retort. . . . For only one part of saltpeter, namely its salt, is not volatile, whereas the other part, that is, the acid spirit, escapes on heating."[1] We meet here a point of view which is akin to that of Paracelsus.

Rudolph Glauber (1604-1670) was prominently active along these lines. Through his writings he exercised a widespread influence. Experimentally he accomplished more than any of his predecessors and also more than many of his successors in the 17th and 18th centuries, by his investigations on the preparation and properties of salts. Through his efforts he added many new salts to the list of those already known. He presented the alchemical theories concerning salts in two publications: "De Natura Salium," and "Tractatus de Signatura Salium, Metallorum et Planetarum."[2] He recognized the point of view of the old philosophers in that "the greatest secretum is hidden in fire and salt," and "that every substance is salt after it has been brought back to the materia prima."

Glauber (like his great prototype Paracelsus) has been sharply criticized in many historical works of chemistry and has been accorded but slight scientific credit. Like Paracelsus he was considered as a kind of "bête noire" in the old chemistry, as an alchemist, adventurer, etc. Such a judgment is surely wrong. Thomson, the English historian of chemistry, is right when he says: "During the seventeenth century there existed several laborious chemists, who contributed very materially by their exertions either to extend the bounds of the science, or to increase its popularity and respectability in the eyes of the world. John Rudolph Glauber is the first of these meritorious men in point of time."[3]

Glauber mentions the following: Sal gemmae or salt (sea salt, rock salt or cooking salt), vitriol, alum, saltpeter, alcalia (fixed salts obtained by leaching wood ashes), and

[1] Ostwald's *Klassiker*, No. 125, p. 4.
[2] Glauber, *Opera Chymica*, I, 441–530 (1658).
[3] *History of Chemistry*, I, p. 226 (London, 1830).

sal ammoniacum. The uses of these six salts are also described. All of them are employed either in "medicine or alchimya." In addition common salt is used in the kitchen, vitriol as a black dye for silk, linen and woolen cloths, alum for dyeing, saltpeter "for the devilish composition of gun powder", the fixed salts for coloring and soap boilers, and sal ammoniacum for the other arts. This statement gives the technical and economic status at that time of the class of compounds called salts. From the theoretical point of view one may find in Glauber's writings many other new and important statements.

It was the method of *synthesis* which enabled him to approach more closely to a true knowledge of the chemical nature and material composition of salts. "The salia fixa (that is, the alkalies and the alkali carbonates) are opposed to the acids (Die Salia fixa seyn den Acids entgegen.)[1] Salts are made up of two different components. Thus sal ammoniacum is derived from sal acidum commune (hydrochloric acid) and sal volatile urinae (ammonia). It can be decomposed to yield these two and can also be synthesized from these two components ($NH_4Cl \rightleftarrows NH_3 + HCl$).[2] In another place he writes: "Thus every sal volatile is different from every spiritus acidus, and a spiritus acidus is opposite to a sal volatile which contains naturam salis tartari. With a spiritus urinae or a spiritus ex sali volatile distillato, metals which are dissolved in spiritibus acidis can be precipitated as with liquori salis tartari." In accordance with our modern nomenclature this statement can be interpreted as follows:

1. Every volatile base, such as ammonia, may be contrasted chemically with every volatile acid (such as HCl, HNO_3 and H_2SO_4), and vice versa.

2. The volatile base possesses the same chemical properties as an alkaline potash solution (potassium carbonate) as both precipitate dissolved metallic salts in the same way.

[1] Glauber, *Furni . . .* II, p. 164 (1648). Acidum, acid, is used here as the geneicr term denoting the opposite of alkali. Glauber's point of view anticipates that of Tachenius.

[2] Idem, *op. cit.*, p. 163.

Another example is that of saltpeter, "namely, that the liquor fixus (dissolved potash, potassium carbonate) and spiritus acidus nitri (nitric acid) are in their nature . . . totally unlike, foes and adversaries of each other . . . and when the two are brought together again . . . and the one part has overcome and killed the other, neither a fiery liquor nor a spiritus acidus is to be found in their dead bodies, but the same has again been made, as both were before and from which they were derived, namely ordinary saltpeter."[1] Potash was obtained from saltpeter by reduction with charcoal; nitric acid, from saltpeter by distillation with "bolus" or clay. In the same way ammon saltpeter[2] can be synthesized from ammonia and nitric acid; potassium sulphate from tartar salt (Weinstein, potassium carbonate) and vitriolic oil (sulphuric acid).

Point of saturation.—How the saturation and neutralization point was recognized in the synthesis of these salts from potassium or ammonium carbonate and free acid, is a question whose solution is quite interesting. A case which well illustrates the process is the saltpeter synthesis. A definite quantity of rectified "spiritus acidus nitri" (nitric acid) is first prepared; then a filtered solution of nitrum fixum (potassium carbonate) or "liquor nitri fixi." "The liquor nitri fixi is then added drop by drop to the spiritus nitri until no further effervescence is produced, until both disagreeable natures—the spiritus acidus and the liquor fixus nitri—have killed each other and the spiritus corrosivus has lost its corrosive properties and the fiery liquor its fiery characteristics, that is, until natural saltpeter again has been formed from both."[3]

This statement can be expressed more understandingly by the simple modern equation

$$K_2CO_3 + 2HNO_3 = 2KNO_3 + H_2O + CO_2$$

The formation of the neutral nitrate is complete when the salt, potassium carbonate, has been converted and all

[1] *Pharamacop. Spagyrica*, p. 48.
[2] *Furni*, II, 170.
[3] De Signatura Salium, cf. *Opera Chymica*, I, 52 (1658).

carbonic acid has been given off with effervescence. Glauber makes use of a titrimetric method in which an acoustic indicator (the "effervescence" of the escaping carbon dioxide) serves for the recognition of the end point of the reaction. Therefore, in a practical way, he recognizes the condition of neutralization or limits of saturation of salts. Abstractly he links this state with the disappearance of the opposite characteristics of acid and base.

This dualistic point of view of the chemical composition of salts in the case of the afore mentioned substances served as a useful working hypothesis in the hands of Glauber. Further than that it has been of fundamental importance in other respects. For all later scientific theories concerning the binary nature of salts are based on the principle of oppositeness, of contrast or polarity, whether they be called basic or acid, positive or negative. Glauber even splits up the vitriols, copper sulphate and ferrous sulphate, in accordance with the dualistic principle. "Common vitriolum is really composed of a sulphuric salt [H_2SO_4] and earths containing[1] iron and copper [FeO and CuO]."[2]

Purification.—Another important step in the history of the development of the views concerning salts is the elaboration of the ideas concerning the individuality, the purity of the various salts. What characteristics were possible in that old time and which of them were used by Glauber in his investigations? From his writings one can plainly see that he recognized the practical significance of the purity of salts and acids, and that he advanced this idea especially where these substances were to be used subsequently in medicine and chemistry. Repeated distillation, yes, even separate treatment of the various volatile fractions (spiritus → phlegma → oleum), is advised. In the case of the salts and vitriols, repeated solution, filtration, evaporation and crystallization are employed. Occasionally, if these processes do not lead to the desired degree of

[1] Special attention should be given to the view that vitriols are composed of earths "containing iron and copper." This was a distinct advance (cf. Biringuccio, *supra* p. 29).

[2] Pharmacop. Spagyrica, cf. *Opera Chymica*, I, p. 72.

purity, an interesting roundabout way is employed. For instance common salt is not freed from its "terrestrial matter" by a mere recrystallization from water, but is dissolved in "its own spiritus," that is, hydrochloric acid, then filtered and recrystallized. Saltpeter(KNO_3), prepared by various methods, is obtained absolutely pure by Glauber's method. According to his directions it is first reduced to the carbonate by fusion with charcoal. The resulting product is then dissolved in water, the solution is filtered, and pure nitric acid is then added to the filtrate until effervescence has ceased.[1] $2HNO_3 + K_2CO_3 = 2KNO_3 + CO_2 + H_2O$. The hygroscopic properties of calcined tartar or nitrum fixum (K_2CO_3), and calcined vitriol ($FeSO_4$) were recognized by Glauber, who employed these substances for the dehydration or rectification of the aromatic oils, spiritus ardens ex vino, etc.[2]

Indices of purity, and Identification of salts.—Glauber recommends as a perceptible proof of purity, the characteristic crystal form of the salt. He describes the crystal form of the purest states.

Common salt (NaCl)—fine granules, crystallized in quadrangular forms like cubes, as if they had been drawn with dividers.[3]

Saltpeter (KNO_3)—"crystals . . . small or thin, yet also elongated without points . . ., but even and alike, as if they had been planed into long hexagons."

Potash (K_2CO_3)—"like small stars, also hexagonal, circular, every point spaced evenly as though laid by the aid of a pair of dividers."

Vitriol and Alum—not opaque lumps, but bright and crystalline, similar to common salt, also cubical.

Sodium sulphate, Glauber's salt (Na_2SO_4)—"elongated crystals like saltpeter, clear and transparent."

Glauber also devotes some attention to the symbolic representation, the signatures, or chemical signs of the

[1] *Opera Chymica*, I, p. 253 f. (1658).
[2] Ibid., p. 90.
[3] *Opera Chymica*, I, p. 489.

salts.[1] He reproached his contemporaries because they had introduced arbitrary signs and "characters," every "chymicus" after his own manner. He discards the sign for salt ⊖ and saltpeter ⊙. For, if common salt is carefully purified "it is obtained in its right sign, namely, in the form of a rectangle." The most highly purified saltpeter is "narrow or thin, but elongated and without points . . . which therefore represents the natural symbol for saltpeter." The symbol for a salt should therefore represent its crystal form when in the pure state.

The whole work of Glauber on salts may be summed up, step by step, as follows: first, his efforts and his success in increasing the number and kinds of salts; his delight in experimental work which caused him to look for the practical applications of these salts in medicine and everyday life. At the same time the increased number of these salts led to a determination of indications of their *purity* and *individuality*. Quite subconsciously does the fact then come to light that each "salt" has its own type and properties and always exhibits these properties, no matter how it may have been prepared. Thus, natural sal ammoniacum and synthetic ammonium chloride (from NH_3 and HCl) are identical, as are natural saltpeter and the synthetic saltpeter obtained from tartar salt (K_2CO_3) and spiritus nitri (HNO_3). This is the principle of the "conservation" (or constancy) of the chemical type or individuality. The important conceptions of Glauber were formed before the appearance of R. Boyle's works. The recognition of these facts leads to the question as to the chemical composition of the individual salts. It follows by direct analysis and synthesis that the structure of salt is made up of two chemically opposite parts—an alkali (base) and an acid. Briefly we may say that a salt is a compound product generated by the interaction of an acid, whereby the specific properties of both are destroyed ("killed").

[1] De Signature Salium, cf. *Opera Chymica*, I, p. 522 ff (1658).

III. THE PERIOD OF THE PHLOGISTON THEORY (ca. 1700-1780)

Let us next take up chemistry as it was known about the year 1720 and ask the following question: What were the opinions of George Ernst Stahl (1660-1734) the great medical man and foremost chemist of this period, noted as the founder of the Phlogiston theory? To characterize the scientific position of Stahl let us quote an objective opinion. The famous historian of chemistry, Thomas Thomson, calls Stahl "one of the most extraordinary men whom Germany has produced, a man who in spite . . . of the barbarity of his style, raised himself to the very first rank as a man of science, and had the rare or almost unique fortune of giving laws at the same time to two different and important sciences, which he cultivated together. . . . These sciences were chemistry and medicine."[1] Stahl studied medicine at Jena, was (1694-1716) professor of medicine at Halle, and (1716-1734) in Berlin physician to the King of Prussia. The general idea of Stahl's medical theory was that he resolved all diseases into the actions of the soul, which is the ruler and regulator of the body, and therefore exerts itself to restore the functions of the body, when these are deranged. It seems that such a view of the rôle of the soul in disease is very modern. (Think of the psychic influence, the mind cures, of Coué and the many followers of psychotherapy!) What did he have to say concerning salts, acids, and bases?

"According to their own nature salts are of a fluid consistency, moderately volatile and corrosive, soluble in water." (Evidently the liquid acids also are called salts).

"After they have been allowed to come into contact with certain earthy matters and have gnawed them, various kinds of salts may form. The most common ones are those which are found occurring in nature, such as common salt, saltpeter, alum, vitriol, rock salt, and sal ammoniac."

"These salts cannot be differentiated from one another in their coarser form except according to the various kinds

[1] Thomson, *History of Chemistry*, I, p. 250 (London, 1830).

of earth and of mixed earthy bodies which they have gnawed, with which they combined to form denser substance. One must furthermore note that one such earthy Concretum draws, envelops and holds much more strongly the saline substance than another, from which it follows that it gives up the one more, or less, readily than the other."[1]

First of all, the purely mechanistic explanation of the mode of reaction of acids upon "earthy matters" must be emphasized. The use of such words as "gnaw" and "envelop" is reminiscent, indeed, of Lemery. One should also note that the "earthy matters" and not the acids are to be regarded as the characteristic parts of the salts. Furthermore, the acids are counted among the corrosive and fluid salts.

The question of the constitution of acids and bases was settled at the very beginning according to the Phlogiston theory, the theoretical views of that time representing the complete antithesis of our present day ideas. Now, as then, the elements or undivided substances are the standards for comparison. Formerly one said:

Compound		*Simple constituents*
Sulphur	=	sulphuric acid + phlogiston
Phosphorus	=	phosphoric acid + phlogiston
Lead	=	lead oxide + phlogiston

Sulphuric acid, phosphoric acid, phlogiston—these were the undivided or elementary substances. To-day we say just the opposite, that:

Compound		*Simple substance*
Sulphuric acid	=	sulphur + oxygen + hydrogen
Lead oxide	=	lead + oxygen

Just as we are, at present, certain that lead oxide contains lead and oxygen, just as certain did it seem, about 1650, that potassium sulphate was composed of potash and sulphuric acid. It could be obtained from alkali (K_2CO_3) and sulphuric acid as "sal duplicatum." (Crollius, Tachenius, Stahl). Phlogiston could convert it into potassium sulphide which means that it is reduced by charcoal. Further-

[1] Stahl, *Chymia Rationalis et Experimentalis*, p. 106 (Leipzig, 1720).

more potassium sulphide could be obtained directly from alkali and sulphur both by dry and wet methods. Sulphur, as well as its basic principle "sulphuric acid," is therefore common to potassium sulphide, oil of vitriol, and potassium sulphate.

Although Lemery in 1675 probably knew of the terms acid, acidum, l'acide, he nevertheless designates the individual acids as "spirits," for instance, esprit de nitre (HNO_3), esprit de sel (HCl), esprit de vinaigre (CH_3COOH), esprit de vitriol and huile de vitriol (H_2SO_4), and describes their properties very accurately. However, the terms acidum nitri, acidum salis marini were already used by Boerhaave in 1732.[1]

This transition from one terminology and conception to another, as illustrated in the case of the two above mentioned, widely known textbooks, had already taken place in several special investigations. Thus we find that Geoffroy the elder,[2] in his paper on the "Table de différents rapports observés en chimie entre différentes substances" (1718), employs the terms "acide du sel marin," "acide nitreux," "acide vitriolique," (but "esprit de vinaigre" is used for acetic acid). Geoffroy also mentions the solid alkaline salts (sel alcali fixe), the volatile salts (sel alcali volatile), the absorbent earths ("terre absorbante," probably referring to the alkali carbonates, clay, lime, etc). Very remarkable is his definition of several salts which were prepared by the action of acids on earths and metals. The process referred to in the following quotation involves the preparation of corrosive sublimate from calcined vitriol, fused common salt, and mercuric nitrate. He says: "The vitriol which is an intermediate (neutral) salt derived from vitriolic acid and iron. The latter substance dissolves in the acid and is linked very closely with it. Common salt is also an intermediate salt, which is composed of hydrochloric acid and an earth which is strongly bound to it. Nitrous mercuric salt consists of nitric acid and mercury."

[1] Boerhaave, *Elementa Chemiae*, p. 813 (1732).

[2] Stephen Francis Geoffroy was born in Paris 1672, studied pharmacy, was made Professor of Medicine in 1709, died 1731. Was a member of the Academy.

Remarkable, indeed, is the knowledge in 1718 of the material composition of salts, or the very clear connection of the various types of salts with substances from which they are derived. Thus,

vitriol = vitriolic acid + iron
nitrous mercuric salt = nitric acid + mercury
common salt = hydrochloric acid + absorbent earth.

It was Rouelle, however, who carried these facts to fuller development. Rouelle introduced new ideas and terms into the chemistry of salts. A neutral salt, he writes, is "a salt formed by the union of an acid with any substance whatever, which serves as a base for it and imparts to it a concrete or solid form", or "neutral salts are formed by the union of acids with alkalis, they are soluble in water, and imprint on the tongue a saline taste." He says further, "The number of neutral salts was at first very small, scarcely any were known but sea-salt and nitre; but the number was soon increased, above all by the work of Glauber. Others have since been added of which the bases are the volatile alkali and an absorbent earth. Finally there have been added salts formed by the union of acids with metallic substances."[1]

There are several facts in this quotation which are noteworthy: first, the concept "neutral salt," secondly, the characterization of a salt by its solubility in water, thirdly, the crystalline state and special taste of salts, and last, but most important, the attempt to characterize chemical constitution by introduction of the term "base" of a salt.

In his paper published in 1754, Rouelle is the first to distinguish between "sels neutres ou moyens," "sels acides," and "sels avec excès de base." Two reactions are thus indicated for the method of formation and the composition of salts, namely,

(1) Acid + Base = Salt
(2) Acid + Metal = Salt

Information concerning the meaning of the term salt, acid and base about the year 1750, can also be obtained from

[1] Mém. de l'acad., 356 (1744); and 572 (1754).

a publication by Wm. Lewis.[1] We here find the statement: "Acids, are all those things which taste sour upon being reduced to a proper degree of strength; as vinegar, juice of lemons, oil of vitriol, etc., and which effervesce with chalk, and the salts of vegetables prepared by incineration; and with such like substances form a neutral salt. They are likewise distinguished from alkalies, by turning syrup of violets red."

"Alkali, is any substance, which being mixed with an acid, ebullition and effervescence ensue thereon, and which afterwards forms a neutral salt. They are likewise distinguished from acids by turning syrup of violets green."

"Neutral salts are a sort of intermediate salts between acid and alkali, and though composed of both, yet upon trial, exhibiting the marks of neither one nor the other."

The character of a salt is most aptly illustrated by the following statement: "Sugar. It is the essential salt of a reed. . . . Sugar, like other salts, readily dissolves in water, and in a certain quantity of it, shoots into regular crystals, of a prismatic figure". Solubility in water, crystal form, and indifference towards plant dyes are, therefore, the chief properties of "salts." Acids and alkalies are differentiated by their opposite behavior toward plant dyes, and by the fact that upon interaction these opposing characteristics disappear in the formation of a neutral salt. Even crystallized sugar is regarded as a salt.

Even as late as 1781 Cavallo[2] defines a salt as follows: "Salts or salty substances are those bodies which are soluble in water and possess a taste. From the point of view of heaviness and ability to withstand fire they may generally be placed intermediate between the purest earth and water." Regarding acids and bases he says: "Many great chemists have believed that all acids are only modifications of a single one. . . . From this it would follow that with the aid of suitable means one acid might easily be transformed into another."

[1] *A Course of Practical Chemistry* (London, 1746).

[2] Cavallo, *Treatise on the Nature and Properties of Air* (London, 1781); (Ger. tr., Leipzig, 1782).

"Acids, alkaline salts, and compounds of both, when they appear in concrete form, are salts, and of the purest kind."

"Although various kinds of alkaline salts are mentioned, only one alkaline principle is assumed to exist in nature. This one principle has, in combination with certain substances, various special properties."

In this definition, as given at the end of the 18th century, we witness a return to a theory which, as we have already learned, was a dominant thought at an earlier period, that of Lemery, 1675. This theory assumed, as a fundamental thought, that all acids contained a common material constituent, that they were derived from one "proto or primary acid," that they could, therefore, be changed one into another.

We shall soon hear about Lavoisier's theory in which oxygen takes over the rôle of acid principle. Think of the present day theories which regard the hydrogen ion as the common material basis of all acids. And think of our methods of oxidation or reduction or substitution (in inorganic and organic chemistry), by which one acid may "be transformed into another."

Equally as interesting is the idea of a common principle inherent in all bases. Is not this old conception reminiscent of the present-day hydroxyl ion which, in combination with different metallic ions, gains "various special properties"?

Let us take the quotations from Cavallo's book on "salts, acids and alkalies" as the final point in the long line of development, both of the chemical facts and views in old days. The experimental work of many centuries has brought rich fruits. The chemist's mentality has been perfected and its emancipation from the former animistic prototypes has been achieved. The old terms in respect to chemical actions and qualities, like 'to devour', 'kill', 'gnaw', 'infect', were discarded and new names and aims came into use. We leave a millennium of chemical efforts and enter into a century which is characterized by the eminent rise of chemical knowledge and power.

IV. OXYGEN AS THE MATERIAL PRINCIPLE AND DETERMINANT OF "ACIDS" (LAVOISIER)

A new phase in the understanding of salts, acids and bases is linked to the name of Lavoisier. However, he did not reach in his investigation the unparalleled accuracy of a Cavendish, or the eminent productivity of the discoverer Scheele. He excelled, like Priestley, in a quite unusual mental alertness, and he possessed special facility in organizing and coördinating heterogeneous chemical observations. In these respects he surpassed his famous predecessors and contemporaries, and created a new kind of chemical theory and experimental technique. He not only inaugurated a chemical revolution by the oxygen theory that he brought forward, but he also markedly advanced the science when he expressed chemical reactions by mathematical equations and when he, together with Morveau and Fourcroy, created a rational chemical nomenclature. In the year 1787 Lavoisier wrote as follows: "Toute science physique est nécessairement formée par trois choses: la série des faits qui constituent la science, les idées qui les rapellent, les mots qui les expriment. Le mot doit fait naître l'idée, l'idée peindre le fait; ce sont trois empreintes d'un même cachet."[1] The abundance of new facts brought out by the discovery of several new gases, particularly oxygen, thanks to the labors of Black, Priestley, Scheele and Cavendish, required new ideas, new conceptions and a new terminology. Just as Stahl, on the basis of his phlogiston theory, had made combustion phenomena the most important field of research, so did Lavoisier now regard oxygen as the most important element in chemistry. The name which he gave to the "spiritus nitro-aerius" of Mayow (1674), to the "dephlogisticated air" of Priestley (1774), and to the aër vitriolicus" or "fire air" of Scheele (1771), signifies a new chemical doctrine. In 1777 Lavoisier published an article entitled "Considérations générales sur la nature des acides" in which he gives the "pure air" derived from

[1] "Every physical science must rest upon three things: the facts which constitute the science, the ideas which recall them, and the words which express these facts. The word ought to call forth the idea, the idea depict the fact. They are three impressions stamped with the same seal."

mercuric oxide the name "oxygène" (ὀξύς = sour, γεννάω = I make), meaning "générateur de l'acide, principe acidifiant." In other words oxygen is regarded as the substance which imparts acidity or acid character to all acids.

What is the composition of acids? Lavoisier (1787) gives the following answer: "Les acides sont composés de deux substances de l'ordre de celles que nous regardons comme simples: l'un qui constitue l'acidité, c'est de cette substance qui doît être emprunté le nom de genre; l'autre qui est propre à chaque acide, qui les différencie les uns des autres, et c'est de cette substance que doît être emprunté le nom spécifique."[1] Acids, then, are binary compounds one of whose two elements is always oxygen, the "principe acidifiant," while the other represents the "base acidifiable" or the acid radical. Among such simple "bases" or "radicals" of the acids were included (1787): "Azote ou radical nitrique," "Carbone ou radical carbonique," "Soufre ou radical sulfurique," and "Phosphore ou radical phosphorique."

Acids	= *Radical*	+ "*Acidifying Principle*"
Sulphuric	= Sulphur	+
Phosphoric	= Phosphorus	+ Oxygen
Carbonic	= Carbon	+
Nitric	= Nitrogen	+

Hypothetical radicals were assumed for acids derived from the plant and animal kingdoms. The somewhat hazy relationships in the case of the four elements just mentioned were subsequently applied to the numerous organic acids whose make-up had hardly been investigated. Without hesitation radicals were promptly assigned to succinic, acetic, formic, oxalic, benzoic, malic and other acids. It is obvious that these generalizations were carried decidedly too far, so that the sure basis of fact and reality were abandoned altogether. Whereas the specific proper-

[1] Acids are composed of two substances of the order of those we regard as elements: from the one to which the acidity is due, should be derived the generic name; from the other substance peculiar to the acid and differentiating one acid from another, should be derived the specific name.

ties of acids had previously been deduced from their behavior in aqueous solution, now the anhydrous oxygen compounds were to be put into the class of acids, as for instance sulphur plus oxygen to form sulphuric acid. The term "base" introduced by Rouelle as a fundamental constituent of salts (acid + base = salt) receives a somewhat different meaning through Lavoisier's conception "base acidifiable" (acidifiable base + oxygen = acid).

Besides the acids, there are also oxygen compounds of metals which are not acids; these are given the name "oxides." In addition there are also the alkalies and earths which belong to a group of "substances which have not yet been decomposed." Neutral salts consist of the following three components, (1) a "principe acidifiant" (oxygen), common to all, (2) a "base acidifiable" (a "radical" such as sulphur, phosphorus, etc.), characterizing a particular acid, and (3) the saline, earthy, and metallic foundation which determines the nature of the salt.

Salt = Radical (base acidifiable) + Oxygen + Salinic Radical (an earthy and metallic basis).

In addition to the oxygen theory of acids, Lavoisier, de Morveau and de Fourcroy worked out and proposed a "Méthode de nomenclature chimique" in 1787. This new, rational, French system of nomenclature aimed to take into consideration the hypothetical deductions concerning the nature and composition of individual substances. It was so masterly in its broad aspects that it is still applicable today in the case of simpler inorganic compounds, and has largely served as a pattern for chemical expression in other languages. To illustrate: Acide sulfurique, sulfate; sulfite, acide sulfureux; sulfure, carbure, phosphure; acide nitrique and acide nitreux, nitrates and nitrites; acid carbonique, carbonates.

V. HYDROGEN AS THE MATERIAL PRINCIPLE AND DETERMINANT OF "ACIDS" (DAVY)

Lavoisier's theory of oxygen acids was of importance because it served to systematize the oxides and helped to create a rational nomenclature. The division of oxides into

acids and non-acid metallic oxides is in itself a contradiction of the fundamental idea that oxygen is the "principe acidifiant." Furthermore, there was the substance chlorine, discovered by Scheele in 1774 which was obtained from hydrochloric acid as a yellow-green gas, "dephlogisticated marine acid." Lavoisier gave to hydrochloric acid the name "acide muriatique" (latin, muria = salt), and since all acids were thought to contain oxygen, it was assumed that hydrochloric acid was composed of oxygen and a hypothetical radical, that is a "base muriatique" or a "radical muriatique." According to Lavoisier, Scheele's gas was a combination of oxygen with hydrochloric (or muriatic) acid. We may say, therefore, that

hydrochloric acid = oxygen + murium (base muriatique)

and that Scheele's gas, or

chlorine = (oxygen + hydrochloric acid) = (acide muriatique oxygéné or oxymuriatic acid).

It was Davy who, by a series of careful investigations begun in 1810, cleared up this whole question and defended his ideas on the matter against Berzelius. In 1810 Davy concluded from his experiments that "muriatic acid may be considered as having hydrogen for its base and oxymuriatic acid as its acidifying principle."[1] With regard to the latter he stated very definitely in 1811 that "at present we have no more right to say that oxymuriatic gas contains oxygen than to say that tin contains hydrogen; and names should express things and not opinions; and till a body is decomposed, it should be considered as simple." Davy proposes the name "chlorine" (Χλωρός = yellow) for "oxymuriatic acid" as "a name founded upon one of its obvious and characteristic properties—its color."[2] It follows from Davy's views that the composition of hydrochloric acid and its derivatives may be represented by the equations—

[1] Trans. Roy. Soc. London, 231 (1810).
[2] Trans. Roy. Soc. London, 1, 155 (1811).

muriatic acid = hydrogen (one volume) + chlorine (one volume)
muriate of potash = potassium + chlorine,
oxymuriatic acid = chlorine = simple body (element),[1]

These views were not accepted by Berzelius who presented the following equations:
muriatic acid = oxygen + a combustible radical (still unknown)
muriate of potash = muriatic acid + potash
potash = oxygenated compound of potassium.

Berzelius, consequently, became the defender of the classical oxygen theory of acids as promulgated by Lavoisier. The point of view of Davy seemed to him to be so improbable that he could not conceive that it "could ever gain credit" (1813).

A characteristic episode in the development of views on acids and alkalies may be mentioned. At that time both physicists and chemists took part in this scientific dispute in which the differences between acid and base became greater and greater. We witness a curious epoch in the development of the views on acids and alkalies. The question as to whether oxygen or hydrogen is the distinguishing element was temporarily relegated to the background by the more important question: "Is there really any such thing as acid or alkali?" Avogadro[2] differentiated between acid and alkaline antagonism: "What we regard as definite acids and bases, are, accordingly, only substances which possess an alkaline or acid antagonism with reference to other bodies . . . The word acid refers only to an accidental property of a substance," and furthermore, "the word can no longer be employed as a generic term."

The famous Danish naturalist Oersted (1812) held similar views concerning acids and bases. Acids may be recognized only because of alkalies, and vice versa. Both conceptions are only relative. Consequently it is suggested

[1] It may be of interest to remember that chlorine as a revolutionary factor in chemistry, destroyed not only the oxygen theory of acids, but likewise, at a later period, the electrochemical dualistic theory of Berzelius. Consider in this connection the discovery of the substitution of hydrogen by chlorine (Dumas).

[2] Gilb. Ann., 34, 64 (1810).

that it would be best to compare the behavior of a certain substance with a standard such as nitric acid, or ammonia.

The ideas of Gay-Lussac[1] are also of the same nature. He said in 1814: "For many years I have regarded an acid, taking the word in its widest sense, as nothing more than a body which neutralizes alkalinity. It is of no importance, if this body contains or does not contain oxygen. Acidity and alkalinity are properties which are related interchangeably to one another, one of which can be defined only through the other. Thus the oil in soaps behaves like an acid, because it satisfies the alkalies. In several ethereal substances alcohol behaves as an alkali, because it satisfies acids." "One is forced to explain the acidity by the fact that it satisfies alkalinity, because acidity and alkalinity are two correlated and inseparable properties." "The supposition seems more and more justified that the neutral, alkaline, or acid character of a compound is not alone a function of the character of its components, but is also dependent upon the quantity[2] relationships and upon their special condensation; in other words, upon the arrangement of their particles (de l'arrangement de leurs molécules)."

Let me particularly call to your attention the similarity in the definition of acids and bases by Avogadro, Oersted, and Gay-Lussac. The old conception of oppositeness or polarity advanced in early days by Glauber and Tachenius, again reappears. Alkalinity and acidity are only relative, only "correlated, inseparable properties" of matter which are reciprocally determinant and dependent. Not so much the chemical character of the components as rather the "arrangement of particles," that is, the spatial relationships, are the deciding factors which determine in which of the two ways a substance will act. One is almost tempted to pronounce these theories in many respects as old (Lemery, 1675) and at the same time as entirely modern!

It should be noted that Davy himself wrote in 1814 "that acidity does not depend upon any peculiar elemen-

[1] Gilb. Ann. d. Phys., 48, 341 ff. (1814).

[2] Indeed, in these views Gay-Lussac anticipated the results of our modern measurements; the affinity constants rise in the order $HClO_1 < HClO_3 < HClO_4$, or $H_2SO_3 < H_2SO_4$, or $HNO_2 < HNO_3$.

tary substance, but upon peculiar arrangement of various substances." However, new facts soon were added, and the discussion returned to the former lines of reasoning.

In 1811 Courtois had discovered iodine. Three years later Gay-Lussac[1] discovered hydriodic acid, recognizing it at the same time as an analogue of hydrochloric acid. In pointing out that the substances formed by combination of iodine, chlorine, or sulphur with hydrogen were just as much to be considered as acids as those containing oxygen, he proposed the prefix "hydro-" for the former to differentiate them from the latter ones containing oxygen, viz. hydrochloric, hydro-iodic, hydro-sulphuric acids. In 1815 he added another acid, hydrogen cyanide, to this group of hydro-acids, giving it the name "l'acide hydrocyanique," a name which has been retained in the nomenclature of the present day. To justify this, he made the assumption that the cyan radical was similar in its behavior to chlorine, iodine, and sulphur.

At about the same time a typical organic acid, oxalic acid, was placed in the same class with the halogen acids. On the basis of Dulong's investigations (1813-1815) on oxalic acid and its metallic salts, L. Gmelin[2] expressed the opinion that pure anhydrous oxalic acid consisted of hydrogen, carbon and oxygen, but that in metallic salts it was composed only of carbon and oxygen.

The discovery of bromine by Balard in 1826 soon yielded another oxygen-free acid, hydrobromic acid. If we include thiocyanic acid, hydrogen selenide, and hydrogen telluride, which had in the meantime been discovered, there were known in 1830 the following oxygen-free acids

$$HCl,\ HBr,\ HI,\ HF,$$
$$HCN,\ HSCN,$$
$$H_2S,\ H_2Se,\ H_2Te,$$
$$H_2SiF_6,\ HBF_4$$

What common constituent did all these acids possess, if they no longer contained the old Lavoisian acid principle oxygen? The answer could only be—hydrogen!

[1] Ann. chim. phys., 91, 5 (1814).
[2] Gmelin, *Handbuch der theoretischer Chemie*, II, p. 1696 (1822).

The hydrogen acid theory of Davy was consequently supported by a large number of examples. Those given above were, of course, inorganic in nature. What about organic acids?

VI. THE VIEWS OF BERZELIUS

For clarification of this question we must turn first to the views of Berzelius. This investigator, logical defender of the classical oxygen-acid, or radical, theory, was also the sagacious co-founder and developer of the newly arisen organic chemistry.

A hundred years ago he described acids, bases, and salts in the following manner:

"An oxide may be called an acid if it possesses a sour taste and has the property of changing various blue plant dyes, such as those obtained from litmus or violets, to red. In spite of the fact that the acidic properties of a substance may vary with the nature of the acid, even to the extent that the acid properties may entirely disappear, as in the case of silicic acid, they may nevertheless still be called acids if they are able to combine with the oxides of electropositive metals, that is, with salt bases, to form salts. It is this latter property which chiefly characterizes acids."[1, 2]

Berzelius gives the following definition of bases. "Bases are electrochemically the opposites of acids, and one includes in the category all those substances which remove the acid properties from acids and from salts of them. A base is therefore an alkali, an earth, or distinctive sort of a metallic oxide. The name rests on the fact that one regards bases as the characteristic components of salts."[3]

Note the fact that bases, like acids, were regarded by Berzelius as anhydrous oxides. The following are some equations given by him in his publication, "Versuch über die Theorie Chemischer Proportionen, etc."[4]

[1] Berzelius, *Lehrbuch der Chemie*, I, pt. i, p. 445 (1825).

[2] This definition was cited recently by A. Hantzsch as being the best statement of the the actual behavior of acids. See Z. Elektrochem., **29**, 244 (1923), and Ber., **58**, 952 (1925).

[3] Ibid., Vol. IV, Part II, p. 822 (1831).

[4] Dresden, 1820, appendix p. 1ff.

Base + *Acid* = *Salt*

Lime, CaO_2 + sulphuric acid, SO_3 = $CaO_2(SO_3)_2$ = calcium sulphate

Caustic potash, KO_2 + nitric acid, NO_6 = $KO_2(NO_6)_2$ = potassium nitrate

Caustic soda, NaO_2 + acetic acid, $H_6C_4O_3$ = $NaO_2(H_6C_4O_3)_2$ = sodium acetate

Caustic soda, NaO_2 + citric acid, $H_4C_4O_4$ = $NaO_2(H_4C_4O_4)_2$ = sodium citrate

Caustic potash, KO_2 + succinic acid, $C_4H_4O_3$ = $KO_2(H_4C_4O_3)_2$ = potassium succinate

To make these clearer we must understand that the atomic weights employed by Berzelius were very different from what they are to-day. If oxygen be given its atomic weight of 16, then C = about 12, hydrogen = 1, sodium (Na_4) = 92, potassium (K_4) = about 160, sulphur = about 32. The organic acids of Berzelius are our present-day acid anhydrides, viz.,

acetic acid $H_6C_4O_3$ =

$$\begin{matrix} CH_3 - CO \\ \\ CH_3 - CO \end{matrix} \diagdown\!\diagup O$$

succinic acid $C_4H_4O_3$ =

$$\begin{matrix} CH_2 - CO \\ | \\ CH_2 - CO \end{matrix} \diagdown\!\diagup O.$$

To form the neutral salt, two molecules of each of these acids require four atoms of sodium or potassium, or one molecule of the Berzelian bases NaO_2 or KO_2.

These statements may be summarized briefly. Both acids and bases are oxygen compounds or oxides, that is, oxygen has been discarded as the "principle acidifiant." The internal forces which cause an oxide to act as an acid or as a base, are electrochemical in nature.

On the basis of the electrochemical dualism, Berzelius regards as acids those oxides which wander to the positive pole, that is, are combined with negative electricity, while those oxides which combine with positive electricity and

separate out at the negative pole are termed bases. The combination of both is, in general, called a salt, and conversely every salt is broken up by the electric current into its components, acid and base. Thus

electronegative *electropositive*

Sulphuric acid, SO_3 + Potassium oxide, $KO_2 \rightleftarrows$ salt $KO_2 \cdot (SO_3)_2$

The term "amphoteric" was introduced at about this time. This term was first applied to those oxygen compounds which are both acidic and basic, that is, which behave as acids towards bases and as bases towards acids.[1]

A new idea, one which was soon extensively applied in organic chemistry, had its origin in the behavior of phosphoric acid. Berzelius gives the following formulas:

Phosphoric acid = PO_5
Sodium phosphate = $NaO_2 \cdot PO_5$
Calcium phosphate = $CaO_2 \cdot (PO_5)_2$, $(CaO_2)_2 \cdot (PO_5)_3$, $(CaO_2)_4 \cdot (PO_5)_3$ or $(CaO_2)_3 \cdot (PO_5)_2$

It was Thomas Graham,[2] who assigned to phosphoric acid, PO_5, the following formulas, in assuming that it existed in the form of three "acid hydrates."

$PO_5 \cdot 3HO$, $PO_5 \cdot 2HO$, and $PO_5 \cdot HO$

These three modifications of phosphoric acid correspond to three types of salts, in that in each of the acids the hydrogen atoms are replaced by a sodium atom:

$PO_5 \cdot 3NaO$ or $PO_5 \cdot HO \cdot 2NaO$
$PO_5 \cdot 2NaO$ or $PO_5 \cdot HO \cdot NaO$ and
$PO_5 \cdot NaO$

VII. VIEWS OF LIEBIG

This classical investigation of Graham assuredly had its influence on Liebig when he began his study of organic acids. His comprehensive work on the constitution of

[1] Winterl, *Prolusiones ad chemiam Saeculi decimi noni*, 1803.
[2] Trans. Roy. Soc. London, 253 (1833).

organic acids appeared in 1838. In it he renounces the old classical theory of acids as anhydrides, and sets up the hydrogen theory.[1]

Liebig argues as follows: We cannot prove that potassium sulphate contains sulphuric acid, SO_3, and potash, KO, even though we know that SO_3 and KO combine to form KSO_4. What we know definitely are the reactions:

lime + sulphuric acid = calcium sulphate + water

or

lime + hydrochloric acid = calcium chloride + water

Represented in chemical symbols (if O = 16, H = 1, S = 32, Ca = 40, K = 78, Cl = 35.5):

$$CaO + H_2SO_4 = CaSO_4 + H_2O$$
$$CaO + H_2Cl_2 = CaCl_2 + H_2O$$
$$KO + H_2SO_4 = KSO_4 + H_2O,$$
etc.

In conformity with the views of Davy, these reactions are in all cases identical, that is, the metal replaces hydrogen in both acids, forming a salt with the acid radical, while the oxygen of the metallic oxide combines with the hydrogen to form water. Accordingly Liebig defines acids as "compounds containing hydrogen, in which the hydrogen can be replaced by metals."[2] This definition may be represented as follows:

	Acid		*Salt*	
MeO	+ H_2R	= MeR	+	H_2O
Me	+ H_2R	= MeR	+	H_2

Liebig therefore distinguishes three classes of organic acids: those which neutralize one atom of a base, such as acetic and formic acid; secondly, those which unite with two atoms of a base, such as tartaric, malic, and fumaric acids; thirdly, those which combine with three atoms of a base, such as citric and cyanuric acids.

[1] Ann. Chem. Pharm., **26**, 113 (1838); *also* Ostwald's *Klassiker*, No. 26 (1891).

[2] If scientific words and names are to express the facts (as Lavoisier said), there exists a curious contradiction between the name and properties of oxygen. The acidity is not dependent on oxygen as the "principe accidifiant," but on hydrogen; therefore "hydrogen" should be called "oxygen"!

By these generalizations Liebig made a great advance not only in the experimental recognition of the constitution of acids, but also in the theoretical conception of the character of acids and of the formation of salts.

These deductions of Liebig concerning the nature of acids, seemingly so clear and self-evident to us to-day, were by no means so forcefully convincing in 1838. On the contrary, they gave rise to a scientific dispute, whose purely personal aftermath was indeed tragic, as it led to an estrangement between Liebig and Berzelius. As early as November, 1837, Liebig wrote a letter to Berzelius, his friend and advisor, about the beginning of his work on acids, in which he said: "I have let myself in for something which is almost crazy. . . . I am dominated by the idea that all organic acids are hydro-acids in a certain sense." He then develops his arguments and asks Berzelius for his opinion. Berzelius throws the theory aside with the statement that the splitting off of water from salts, "dry distillation," is probably the cause. And he furthermore cautions Liebig against making generalization on the basis of isolated cases. In April 1838, Liebig writes: "I have been living in fear and worry over the theory of organic acids that is developing in me. . . . If sulphuric acid is really $SO_4 + H_2$, then its saturation capacity is dependent only on the hydrogen, which is outside of the radical." Does this not sound distinctly modern, especially when we formulate true acids as $(SO_4)H_2$ or $(CCl_3 \cdot COO)H$? He reports furthermore that he has found it necessary "to establish three classes of acids, namely, mono-, di-, and tribasic acids, one atom of which requires one, two, or three, atoms of base for saturation, in such a manner that for every atom of base one equivalent of water is removed from the acid." Liebig appends to his exposition numerous convincing experiments—and what is the result? How does Berzelius receive it all?

We have in chemistry the van't Hoff-Le Chatelier law which may be stated as follows:—If a system in equilibrium is acted upon by a force in such a manner that the equilibrium is disturbed, the direction of the displacement will be

such as to counteract the force. The same law obtains in the world of ideas and theories, in the living equilibrium of old and generally accepted opinions. The force of new ideas calls forth a counteractance in the balanced system of prevailing ideas. This opposing force may be of varied nature and strength, depending upon the time and cultural level, and upon the inner character of the new idea. The old Greeks offered hecatombs of oxen for new scientific ideas. But even in the same Athens other means were known for checking new ideas, or to cause their reconsideration. Was not the great philosopher Socrates called before the court and condemned to death 399 B.C.? Two thousand years later the philosopher Giordano Bruno was burned at the stake in Rome. The great physicist and astronomer, Galileo Galilei, (1564–1642), was handed over to the inquistorial court at Rome. How fared Robert Mayer, discoverer of the Law of Conservation of Energy, and a contempory of Liebig? His first paper on the fundamental law of thermodynamics was refused for publication in 1841 by Poggendorff, the physicist. Mayer was consigned to an asylum as an incurable lunatic and was placed in a straight jacket. Think of the struggle in 1877 against the stereochemical ideas of van't Hoff and the methods used by his opponents—ridicule and mockery. However, ideas do not perish, nor can they be thrown into prison, nor killed by ridicule! It is true that Berzelius characterized Liebig's acid theory as "absurd" (1838), yet the idea enjoyed a long and successful life. Berzelius harshly rejected the notions of Liebig: "We must aim to make scientific theories as clear as possible, and to change them as little as possible. If, for instance, atoms were increased in size to such an extent that we could see them side by side in $H_2O + SO_3$, and $KO + SO_3$, do you really think that this sight would make clear whether one of the oxygen atoms belonged to the hydrogen or the potassium atom? It seems highly improbable to me." (Does not this idea of 1838 bring to mind X-ray spectrograms and ionic lattices, and do we not believe that we can see where the oxygen atom belongs?) "You have built up an artificial structure which

will topple over at the first scientific blast," wrote Berzelius in his letter to Liebig. Liebig's reaction is given in a letter to his friend Wöhler: "Berzelius slept and we worked; the reins fell from his hands, this awoke him; the lion, whose teeth have become dull, roars, but not even a mouse is frightened by him." Instructive indeed, in this chapter of human, prejudiced opinions, is the enormous consumption of mental energy and acuteness by Berzelius in attempting to prove that something new is absurd, and that a theory which was tottering to its fall was still possessed of full vitality.

Let me briefly summarize the steps in the development of the views concerning "hydracids" or hydrogen acids: About the year 1810 the fact was established (Davy) that there exist true acids which do not contain oxygen. The first important example was hydrochloric acid (HCl). However, Davy himself did not consider chloric acid ($HClO_3$) and iodic acid (HIO_3) as binary compounds, formed by an atom of hydrogen and a compound radical, but as a ternary compound of hydrogen, halogen and oxygen. Nevertheless he distinctly brought out the importance of the hydrogen atom in acids. He rejected (1815) the view that iodine pentoxide (I_2O_5) is an acid, and maintained that it becomes an acid only by combination with water. The first organic acid examined from the new standpoint was oxalic acid. Dulong (1815) examined the salts of this acid and expressed the view that dried oxalic acid must be considered to be a compound containing hydrogen, and that the formation of anhydrous salts from metallic oxides gives water as a result of the union of the hydrogen of the acid and the oxygen of the oxide.

Opponents to these views of Davy and Dulong were Gay-Lussac and Berzelius. Even as late as 1836 Dumas declared that these views must be rejected. Therefore the experimental investigations, speculations and generalizations of Liebig (1838) can be considered as the beginning of

a new era in the conception of acids. Organic chemistry, that new and extremely productive field of research and discovery, profited from Liebig's theory. In connection with Avogadro's molecular theory and the increasing use of the methods of determining molecular weights by vapor densities, the great problem of the "constitution" of the molecules soon became one of the most important features of organic chemistry.

VIII. STATUS OF THE HYDROGEN-ACID THEORY IN RECENT DECADES

The development of new ideas in science is marked by three chief characteristics. First, the compelling steps in the growth of the ideas; second, their own previous history; and third, the influences of the many theories from which they have been crystallized or from which they have been derived, and which they oftentimes refute. Wilhelm Ostwald speaks of them as the "countless inclusions from the mother liquor of the theories of successive ages."

New ideas give a new meaning to previous, experimentally determined facts, and lead to new observations and measurements. Naturally they stand in opposition to the older theories, and since they not only do, but must accomplish more than the latter, they readily are accepted as "explaining" everything. This often causes their supporters to show impatience toward other views, and prejudices their judgment of new phenomena which arise during the progress of chemical experimentation. A theory which had been extremely useful up to a certain time, then begins to have a deterrent influence upon research. Lavoisier's oxygen theory is such an example. But this seems to be the life history of all theories.

What was, in the beginning, the effect of the hydrogen theory with regard to organic chemistry?

Let us quote first the great organizer and systematizer of chemistry, Charles Gerhardt. He defines in his "Introduction à l'étude de la chimie" (Paris, 1848), the subjects under consideration.

Salts. "Nous appellerons sels ou corps binômes tous les composés chimiques formés par deux parties, l'une métallique et l'autre non-métallique, pouvant ainsi s'échanger par double décomposition. En donnant cette définition des sels, nous ne voulons pas indiquer un antagonisme entre les deux parties, tels que l'admet le dualisme électro-chimique."[1]

Bases and acids. "En général, on appelle la base d'un sel le métal ou les métaux susceptibles de l'échange par double décomposition. . . . . Les acides sont des sels dont la base est entiérement formée par de l'hydrogène. . . . . Chaque acide se compose donc aussi d'une partie non-metallique qui varie suivant les genres salins, et d'une partie métallique, l'hydrogène, pouvant être échangée pour d'autres métaux par double décomposition."[2] In addition, acids redden blue litmus and cause effervescence on contact with carbonates; compounds like sugar, which probably form salts, but do not redden blue litmus, are not acids. "Les oxydes salins (potasse, soude, chaux, baryte, strontiane), où un semblable métal forme la base, sont connus sous le nom d'alcalis." From these quotations it is clear that Gerhardt, an ingenious chemical philosopher, brings the complex of problems "salt-acid-base" to one single principle "salt."

August Kekulé, one of the great workers in organic chemistry, widely known through his views concerning the tetravalency of carbon and the structure of benzene, asked the following question in 1858. "What is an acid? Is it a substance whose hydrogen atom can be replaced by metals, or is it one in which this replacement takes place with especial facility? In either case, what are the limits?"[3] Kekulé, as organic chemist, had in mind the behavior of

[1] We will give the name salt or binary compound to all kinds of chemical substances which are formed by two parts, the one metallic, the other non-metallic, both interchangeable by double decomposition. In giving this definition of salts, we do not wish to indicate antagonism between the two parts, such as is admitted by electrochemical dualism.

[2] In general one considers the base of a salt to be the metal or metals which are susceptible of interchange by double decomposition. The acids are those salts, the base of which consists entirely of hydrogen. Every acid therefore is composed of a non-metallic part which varies with the kind of saline matter, and of a metallic part, hydrogen, which can be interchanged for other metals by double decomposition.

[3] Liebig's Ann., 106, 130 Note (1858).

such organic compounds as phenol, acid amides, imides, etc. with reference to the case of replacement of the hydrogen atoms by metals, and the varied stability of the metallic compounds in aqueous solution.

It is worthy of remembrance, when we speak at present of true and pseudo-acids, that Kekulé considered many similar problems decades ago. Such questions as the following were considered: "Is carbolic acid (phenol) an inert alcohol or a monobasic acid?" Kekulé answered the question by saying: "We may assume that there are two different carbolic acids, of which one is a monobasic acid, the other an inert body like alcohol." "The same is true of the amido bodies."[1] The basicity of the monobasic amides is theoretically equal to zero, yet substances like acetamide give salts with monobasic acids. The same is true of the imides, such as hydrocyanic acid. These facts caused Kekulé to advance the question, "What is an acid"?

H. Kolbe[2] formulated the following definition with particular reference to organic acids. "The fatty, aromatic, and related monobasic acids are derivatives of carbonic acid, formed by the introduction of hydrogen or an alcohol radical in place of one of their two extra oxygen atoms." (Carbonic acid was then written as $_2HO(C_2O_2)O_2$.) Original and critical is the point of view taken by him in his "Kurzes Lehrbuch der anorganischen Chemie."[3] Known as a strong defender of the classical trend in chemistry dating back to the time of Berzelius, Kolbe says: "The question 'What is a salt' is no easier to answer than to say what a metal is." "Salts are those substances obtained by combination of acids and bases." "We thus know how salts are formed, but not what they are or of what they consist."

We may also quote from an authoritative text of the time, written by Gorup-Besanez: "We may regard hydrogen as the element which necessarily characterizes all acids,

[1] Liebig's Ann., 103, 180 (1857).
[2] Liebig's Ann., 113, 293 (1860).
[3] P. 391 (Braunschweig, 1877).

because it is a common constituent of all well-defined acids, and because it takes a very active part in the formation of salts."[1]

What does the creator of the periodic system, D. Mendeléeff, say? Like so many other chemists, such as Faraday, Bunsen, and Ramsay, Mendeléeff was interested in organic chemistry in his earlier years, and was the author of a Russian textbook of the subject, which is still worth reading.[2] In the theoretical introduction he discusses as simple "radicals"[3] or elements, such substances as chlorine, hydrogen, oxygen, and nitrogen, and as "compound radicals" the following: SO_2 (radical of sulphuric acid), NO_2 (radical of nitric acid), CO and PO (radicals of carbonic and phosphoric acids, respectively). He characterizes NO_2 as monatomic, SO_2 and CO as diatomic, and PO as triatomic. Then he says, "All acids contain a hydrogen which is easily replaceable by metals or alkali radicals such as ammonium, thereby forming salts. In other words an acid is a salt of hydrogen. Likewise an alkali is a compound which contains a hydrogen atom which may easily be replaced by such acid radicals as SO_2, NO_2, CO, to form salts. A salt may therefore be defined as an acid in which the hydrogen is replaced by a metal or an alkaline radical. Or a salt is an alkali in which the hydrogen is replaced by an acid radical."

$$\text{Acid, } H\text{–}X \longrightarrow \text{Salt } MeX \text{ or } NH_4X$$

$$\text{Base, } MeO - H \longrightarrow \text{Salt } MeO - NO_2 \text{ or } \begin{matrix} MeO \\ \diagdown \\ \quad SO_2 \\ \diagup \\ MeO \end{matrix}$$

Mendeléeff is, therefore, a supporter of the hydrogen theory of acids. He grouped acids and bases under the generic term of "salts," and he held to this concept from 1861 to 1906, presenting it in his famous textbook "Principles of Chemistry," the first edition of which appeared in 1868, the last shortly before his death. In this last edition

[1] *Lehrbuch der anorganscher Chemie*, p. 126 (1871).
[2] First Edition 1861, Second Edition 1863.
[3] For this term compare the nomenclature of Lavoisier.

(1905-06) he defines these terms, ignoring the theory of electrolytic dissociation which he never accepted, as follows: "A salt is an acid, in which the hydrogen has been replaced by a metal." Among the very characteristic properties of salts he mentions their ability "to be more or less decomposed by a galvanic current," and "to enter into double decomposition with other salts." "An acid is nothing more than a hydrogen salt. Water itself may be regarded as a salt in which the hydrogen is either combined with oxygen or with the water residue, that is, the OH group. Accordingly, water is HOH and alkalies or basic hydrates may be represented as MOH." The hydroxyl group may be regarded as similar to the halogen X, like chlorine in sodium chloride. "The alkalies or hydrates of bases are salts of the type MX, composed of metal and hydroxyl, such as caustic soda, NaOH." As a characteristic point in these definitions of Mendeléeff appears the central rôle of the "salt"; acids and alkalies are not special classes of substances, but only special branches of salts. (Ions have no place in his definitions).

Let us also quote Wilhelm Ostwald, a master of theory and a contemporary of Mendeléeff. This famous investigator and teacher says in his "Grundlinien der anorganischen Chemie" (1919):

"Among the numerous compounds of hydrogen there is a large and particularly important class which carries the name of acids. These are hydrogen compounds which are characterized by the fact that hydrogen is removed when metals are allowed to act upon them. . . . Bases are compounds of metals with hydroxyl." He writes further: "The terms acid and base are derived from the fact that substances of the one class have a sour taste and redden litmus, whereas the others are to be considered as the 'foundation' of substances, since they remain behind as non-volatile constituents upon heating."

"The phenomenon which has to do with the fact that certain substances (which shall hereafter be designated as salts) break down, in aqueous solution, into stable components, known as ions, is termed electrolytic dissociation."

On the basis of what has been discussed, K. A. Hofmann defines acids and bases[1] as follows. Laying particular stress on the lability of the acid hydrogen atom, he says "true acids are substances containing a labile, reactive, and replaceable hydrogen; true bases such as the alkalies, *e. g.* KOH, are substances with a labile hydroxyl group capable of forming salts with separation of water."

This definition brings us to the end of a classical, century-long, period of development of the concept "Acid, Base and Salt," a development resulting chiefly from experimental investigations. This definition really contains all the essential, observable characteristics of these substances as they are met with by the organic and the inorganic chemist, and it is thus that they are regarded in present-day theory and research.

At the same time by its qualifying term "true (Echt)" the definition points toward the new, modern, concept that takes account of new experimental facts and new theoretical foundations.

This new phase in the development of the concepts Acid, Base, and Salt, is fundamentally related to electrochemical phenomena. We shall consider them in connection with the concepts "Electrolyte" and "Non-electrolyte."

[1] *Lehrbuch der anorganischer Chemie*, p. 13 (5th ed., 1924).

CHAPTER II

Summary of the Development of the Chemical Views Concerning Salts, Acids and Bases

This historical survey is instructive from many points of view. Let us remember the saying of Goethe: "The history of science is science itself."

When we trace the history of a seemingly narrow, special subject such as acids, bases, and salts, it becomes clear that even this restricted topic stands in a causal relationship to the whole of chemistry, that the particular questions connected with it are directly associated, from period to period, with the state of total knowledge in all divisions of physical science, and that the study of what is apparently a very restricted topic reacts upon the development of allied branches of science.

We have become acquainted with the general results and with the chief investigators in the building up of chemical science, and we have learned something of the rôle that the several men played in the development of scientific views. In this resumé it has been my aim to present chemistry as a living organism and to show in what manner the Past is linked with the Present. The historical study of chemistry is likewise a training of the scientific mind, is a form of mental discipline, and this study demonstrates how consecutive, regular and logical is the growth of scientific theory. We speak sometimes of the "spirit" of a science. This "spirit" is common sense.

Let us follow the development of views concerning acids, bases, and salts, from the side of cognition.

The theoretical views that were advanced show many contradictions in the explanation of observed facts. It was said of Priestley that "no man ever entered upon any undertaking with less apparent means of success than Doctor

Priestley did on the chemical investigation of airs." One might add that no investigator achieved greater success, even though he was unable to present rational theories concerning the very important facts that he discovered.

A man of different type was Berzelius. His maxim was—"We must aim to make scientific theories as clear as possible and to change them as little as possible." In other words a minimum of theories and a maximum of clearness and experimental evidence. A third type of investigator is found in Liebig. Concerning his theory of hydrogen acids he writes: "One may ask whether theory is of value simply because it leads to discoveries. The question is difficult to answer and in the test and use of a new theory one must not be mislead by results. Every new view gives a stimulus toward testing it. It leads to further study. If one works, he is sure to make discoveries no matter where he begins."

One often hears to-day the blunt statement—"that theory is wrong;" but no scientific view is "wrong" if it is based upon actual facts and is reached by logical reasoning. It may be incomplete. It may be based on insufficient data. It may later be refuted by newly ascertained facts, but nevertheless it was true for a given state of knowledge and it often happens that from a new standpoint or in a more advanced period of our science we return unconsciously to former so-called false views and, using new facts, we re-create theories that are analogous to the old. In our historical survey reference has frequently been made to such cases of revival of forgotten scientific ideas; and many of the seemingly original theories of the present day can be traced back to the views of the earlier chemists. Indeed it would appear that the fundamental concepts concerning nature exhibit a law of conservation analogous to the law of conservation of energy.

Furthermore, it is evident that all scientific ideas and theories must have a favorable "culture medium." This brings to mind an old French quotation concerning a famous man which reads as follows: "Il ne suffit pas d'être grand homme, il faut venir à propos." The same thought

might well be applied to a theory. It is quite essential that it appear at the "right time," but it is a difficult matter to ascertain the exact psychological moment for its presentation. It was known in the year 1500 that burning metals increased in weight; Lemery knew in 1675 that the process of combustion was linked with the consumption of something that came from the air. Mayow (1674) knew that a special kind of matter existed in air and gave it the name "spritus nitro-aërius." But not until 1780 did Lavoisier create his oxygen theory. Lavoisier presented his ideas at the proper time! The large collection of new facts and the inadequacy of the traditional views and explanations required the creation of a new idea.

However, a third factor enters at this stage. A new idea needs followers, scientific apostles. It must find mental resonance. The great success of Lavoisier's theory was due not only to its scientific charm and simplicity, but also to the fact that it was accepted by the younger chemists in all countries. The "culture medium" for Liebig's hydrogen theory of acids was certainly his famous chemical laboratory at Giessen. His laboratory was indeed a world laboratory. It attracted students of chemistry from all civilized countries. One could hardly say that the success of Arrhenius' theory of electrolytic dissociation lay in the fact that it was the brain-child of a brilliant physicist. It was the laboratory of chemistry of W. Ostwald which helped to spread his doctrine—a laboratory which was then to modern physical chemistry what Liebig's was to organic chemistry fifty years previous. Ostwald's laboratory was a great collector of mental energy, for to it came the young and talented chemists from all over the world to embrace and become followers of new ideas and methods. Indeed, Ostwald himself was a most clever and indefatigable interpreter and promoter of this theory of Arrhenius, and by his unique and exceptional personality made many scientific converts.

Let us now examine in more detailed form the stepwise development of our special topic "Salts, Acids and Bases." To do this it is necessary to go back even further than the

time of Geber. We find experience and conception limited. Chemical substances and phenomena are expressed and described in an exceedingly primitive manner. No chemical terminology has as yet come into existence. According to the old Greek philosophers the material world was made up of the four elements "fire, water, earth and air." This classification referred not to a difference in the kind of matter, but to one of state. This is evident from a consideration of the three states of matter from the modern point of view as compared to the old terms,—liquid state (water), solid (earth) and gaseous (air). The old chemists for centuries continued to use this elemental classification of substances, and distinguished newly discovered bodies from one another by the use of qualifying terms. Thus liquid substances were given the general name *aqua* plus a characterizing adjective, e.g. *aqua fortis*, *aqua regia*, *aqua dissolutiva*, *aqua vitae;* the earths included all kinds of minerals, stones, ores, and the like; the airs, all sorts of gaseous matter.

The fourth of the Greek elements was "fire." It was the active agent, symbolic of energy in all its forms since it brought about all changes in passive matter, changes of a physical nature as those from solid—to liquid—to gas.

Words were borrowed from the living world to indicate chemical changes in matter. Thus we find expressions such as "killed," "revived," "to gnaw," "saturated," "infected" in the early chemical literature. Simple and humorous as this old nomenclature may have been, it was nevertheless natural and served its purpose for many centuries to follow. It is an indication of the state of knowledge in these past times.

The new era in chemistry had its beginning when the old practical chemists began to study the relationship of different forms of matter, especially the "earths", to the "element water," that is when they began to examine solutions. The earths soon began to be characterized by their behavior toward the two active reagents, fire and water.

The study of water as a solvent led to the first analytical processes by use of the "wet method," as it involved the

separation of the element "earth" into new kinds of earthy matter which were characterized either by their solubility or insolubility in water. These various solubilities are today employed by the chemist in the separation of many earths (oxides) and salts. The dissolved part was found to possess a definite taste, was stable towards fire, and was called a "salt." Further experimentation demonstrated that there were many kinds of salts, viz., common salt, saltpeter, sal ammoniac, vitriols, alums, etc. Their growing practical application and technical value led to more detailed investigations.

The study of the effect upon salts of the most powerful reagent then known, namely fire, led to some of the most important discoveries in all chemical history. New kinds of waters, "corrosive waters" or mineral acids, were formed in this manner. Their isolation may be considered an important step of cognition in chemistry, since it was shown thereby that salts may be decomposed into two components. Thus, following the separation of the element "earth" into a "salt" and an "earthy matter," and the differentiation of the collective salt class into "distinct salts," came the decomposition of every individual salt into a volatile part, or "acid water," "spirit," etc., and a nonvolatile part. Salts were therefore recognized to be binary compounds.

All this new knowledge logically suggested other problems. The question was asked—What are the peculiar properties of these two components and can the original salt be synthesized from them? Analytical operations and synthetic experiments were introduced in an attempt to answer these questions. This investigational work brought forth the opinion that two kinds of matter existed, chemically opposite and antagonistic, which by their reciprocal "killing" (combination) formed a salt. The one was called an "acid," the other an "alkali." The dualistic theory of salts, one which is of fundamental importance in succeeding centuries, had become firmly imbedded in chemistry.

Naturally the old scientists desired to know the cause of the contrasting character of acids and alkalies. Their

line of reasoning probably pursued the following course: All acids show the same chemical and physiological behavior in so far as all have a sour taste and are neutralized or saturated by alkalies. Therefore it is logical to suppose that all acids contain something in common, in other words a specific acid characteristic.

Of course no data were at hand concerning the material or chemical composition of acids. Consequently analogies were sought from among the visible phenomena of the external world. The specific qualities of acids and their particles were compared from a mechanistic point of view as based upon geometrical sizes and forms, viz., points, thorns, screws, etc. The corpuscular theories of Boyle and Lemery were rational answers with regard to the question of causes. Considering the times and the state of knowledge no other answer was possible.

The next stage in the development of chemical science brings to light new facts. Interest is centered around the problems of the conditions of formation and the reversible changes of salts. The theoretical and analytical operations are more widely employed than heretofore. It is observed that the burning of sulphur, carbon, phosphorus, etc., produces acids; that is, that these combustible substances are transformed, with loss of light and heat, into non-combustible products. Considering these facts the conclusion is reasonable that acids are formed by the loss of something, a special inflammable substance, namely, Stahl's phlogiston.

However, the phlogiston theory neglects a fundamental and already well-known fact, it disregards the increase in weight after the loss of phlogiston. If we assume that every increase in weight is caused by the incorporation of a certain quantity of matter, and that the creation of matter during the course of the experiment is excluded, then Stahl's theory is incomplete, for it considers only one side of the problem, that which pertains to the visible emission of "phlogiston," light, or energy.

To do away with this difficulty, Lavoisier substitutes the idea of incorporated oxygen for the expelled phlogiston.

A special kind of matter, an elementary body, becomes the carrier of acidity. All acids, therefore, contain the element oxygen.

With the passing of the antique conception of air as an element, began a new period of chemical thought and experience. Chemists began to use air as a chemical reagent. Just as the study of the relationship of the element "water" to the element "earth" to yield salts, from which were obtained acids, inaugurated a new era and new ideas, so did the investigation of the element "air" lead to the discovery of gases and to Lavoisier's theory.[1]

Direct experimentation was used in an attempt to verify Lavoisier's oxygen theory. It was soon ascertained that two series of facts stood in direct contradiction to it. First it was found that not all substances containing oxygen were acids; on the contrary alkalies and basic oxides also contained this substance. And in the second place, acids were discovered which contained no oxygen at all. Obviously Lavoisier's theory was inadequate. All hitherto existing methods of reasoning had led to the hypothesis that acidity was due to the presence of a certain elemental substance. Consequently Davy advanced the next theory, that the hydrogen atom must be considered the material source of acidity since all acids, both organic and inorganic, contained at least one atom of hydrogen. A new difficulty arose when it was discovered that certain organic compounds containing many atoms of hydrogen (hydrocarbons), displayed no acidic properties whatsoever. Liebig therefore modified the theory by stating that only such substances were acids in which the hydrogen atom is replaceable by metals, *i.e.* the hydrogen atom must be labile and reactive. This latter opinion is generally accepted today.

Let us now turn to the possible future developments of this subject.

[1] It is interesting to note that from the standpoint of the theory of cognition, the development of our chemical sciences was clearly linked to the progressive destruction and analysis of the four elements "water, earth, air, and fire." Scientific analysis and investigation of the element "fire" led to modern thermodynamics.

OUTLOOK FOR THE FUTURE

It seems as though the consecutive steps in the historical development of the concept "acid" fall in line with the gradual change in the point of view as required by a logical consideration of the facts at hand at any particular period of time. Certainly, if such is the case, it ought to be possible to predict or foresee the coming changes concerning these views on acids.

The present definition of acids is hardly satisfactory and comprehensive enough. The question may justly be asked—What is the special state of such an "acid" hydrogen atom? Electrochemistry has undertaken to solve this problem and a consideration of the answer brings us to the discussion of a new and very complicated field of chemistry, namely, that of "electrolytes and non-electrolytes."

We shall learn that the hydrogen atom in acids is present in the ionic state as the cation. But this is hardly sufficient, for there are many organic substances, so-called non-electrolytes, such as ethyl malonate, acid amides, unsaturated hydrocarbons, which can add on metallic atoms or some of whose hydrogen atoms are replaceable by metals. Further, many typical acids such as hydrochloric acid, become non-electrolytes in organic solvents, their hydrogen ions apparently non-existent. Yet they act as acids even under such conditions and undergo reactions of double decomposition with salts.

Therefore even the electrochemical definition in its simplest form is not satisfactory. All that we can say of the "acid" hydrogen atom is simply what we have learned by experiment. It is labile; it can enter into chemical reactions; it is replaceable by metals.

The cause of this so-called lability is a problem which follows logically. Is the hydrogen atom in acids labile, reactive, and replaceable, because of its spatial position, possibly because it is "outside" of the acid molecule? The question would then resolve itself into one of stereochemical arrangement. Or does it owe its characteristic properties to a peculiar state of energy, or "electronic" be-

havior? Or are both of these suppositions simultaneous, actual forces which characterize the acid hydrogen atom?

Another important factor must also be taken into account. We know that liquid hydrogen chloride as such has no effect upon metals; yet when dissolved in aqueous or alcoholic solutions it acts readily enough. Thus, the "acid" hydrogen atom exists in a "potential" state which can only be made active by the presence of a suitable solvent. Hydrogen chloride itself is not an acid. It becomes one only in connection with a solvent.

Naturally the influence of the solvent must also be investigated. Boerhaave once said, "both solvent and solute act reciprocally." If this statement is true, if the solvent influences the physical and chemical action of acids, the fact must exert a profound influence also on dissolved salts.

If the rôle of solvent be studied from the standpoints of the chemist and of the physicist, two different views concerning "solvation" must result. Whereas formerly the hydrogen atom or ion was of primary interest, it is now the molecule in its entirety which becomes the subject of mental analysis. One is struck with the fact that this mode of scientific consideration of acids has many points of similarity with that of Lemery, who sought the cause of acidic properties in the particles themselves.

We can easily imagine that further researches on "acids" will bring the whole problem to a point where such a question as the following will not be at all unreasonable. Is there really any such thing as an acid or an alkali, or are these only accidental properties, the result of specific conditions? The same question was once asked by Gay-Lussac, Avogadro, and Oersted. Another solution is also possible. Chemists may some day prefer to give up all efforts to formulate a general, simple, and exact definition of "salt-acid-base" and restrict this old chemical triumvirate to the single term "salt"—electrolyte.

Be that as it may, the statement of Tyndall will apply always:

"Science is organized common sense."

PART II
ELECTROLYTES AND NON-ELECTROLYTES

CHAPTER III

Electricity and Matter

> "Es würde ja lächerlich sein, die elektrische Materie deswegen für ein Phantom zu halten, weil die Vorstellungen der Naturforscher darüber so verschieden gewesen sind und noch sind." (It would indeed be absurd to consider electric matter as a phantom merely because the conceptions of scientists concerning it have varied and still vary so greatly.)
>
> —Gren, 1794.

> "Das System der Elektrizität wird das System der Chemie werden und umgekehrt." (The system of electricity will become the system of chemistry and vice versa.)
>
> —Ritter, 1798.

REMARKABLE words these, taken from olden times, yet how modern are they in their sense and application. Let us go back to the second half of the 18th century. The knowledge of frictional electricity has already become so extensive that Joseph Priestley compiles a work of several volumes entitled "History and Present State of Electricity" (1767). His compatriot, Cavendish, shows shortly thereafter (in 1775) that nitric acid is formed by passing a spark discharge through air, that is, a chemical combination of oxygen and nitrogen is brought about by electricity. In 1789 the two Dutch investigators, Paets van Troostwÿk and Deiman demonstrate that such electrical discharges can also cause chemical decomposition, water being split up into hydrogen and oxygen. The discovery of Galvani follows in 1791. The end of an old and the beginning of a new and brilliant epoch are marked by

the discovery of the galvanic pile in 1800 by Volta. Ritter (1776-1810), who is regarded by Wilh. Ostwald as the founder of electrochemistry, had already shown that Volta's potential-series of the metals is identical with the affinity-series of these metals to oxygen (1798).

Beginnings of the Materialization and Atomization of Electricity. (Lichtenberg, Davy, Grotthuss, Berzelius)

On the occasion of a critical discussion of the new Lavoisierian system, the sagacious Lichtenberg (1741–1799) spoke somewhat as follows: The general naturalist, who compares and collects isolated activities of single classes, will meet all sorts of difficulties if he attempts to unite this new system with experimental facts which are already at hand about other classes of objects. Nature produces electricity in large quantities, and it is highly probable that it enters into the composition of substances and forms chemical compounds. It may be that it possesses some of the properties which have been ascribed to fire, phlogiston, or light. The chemical relationships of this material should be carefully investigated.

Lichtenberg expresses the opinion in 1780 that "there are two kinds of electricity or two modifications of a single material, which act toward each other as positive and negative values. This, I believe, is true beyond doubt."[1] (About the same time some naturalists described positive electricity as phlogiston and negative electricity as "acid").

Concerning polarity Lichtenberg says, "I believe it is absolutely necessary to investigate what goes on in this world through polarity. I apply this term to a property of matter to combine on certain sides. Something more general seems to lie in this conception than one would ordinarily think."

At the beginning of the 19th century it was customary to list "among the generally distributed elemental substances" the following—heat, light, electricity, oxygen, carbon, etc. Gren discusses these materials in detail.[2]

[1] Lichtenberg, *Vermischte Schriften*, VII, p. 72 (Wien, 1844).
[2] *Handbuch der gesammten Chemie*, II, p. 140–208 (3d ed., Klaproth, Edit., Halle, 1806).

Concerning "electric matter (electrogenium)" he states: "It appears to be widely distributed in nature, but all bodies do not appear to be impregnated therewith in equal degrees." There is thus established the interesting fact that more than one hundred years ago electricity was considered to be a kind of elemental substance (electrogenium) which enters into chemical combinations and forms compounds.

In his Bakerian lecture delivered on November 20, 1806, Davy said: "Amongst the substances that combine chemically, all those, the electrical energies of which are well known, exhibit opposite states . . . It would be useless to speculate on the remote cause of electrical energy or the reason why different bodies, after being brought into contact, should be found differently electrified; its relation to chemical affinity is, however, sufficiently evident. May it not be identical with it, and an essential property of matter? . . . Allowing combination to depend upon the balance of natural electrical energies of bodies, it is easy to conceive that a measure of the artificial energies may be found . . . and such a measure would enable us to make a scale of electrical powers corresponding to degrees of affinity."[1]

As one of the judges in the award of the "Galvanic Prize" founded by Napoleon, to Davy, Gay-Lussac expressed himself as follows concerning the latter's views: "The idea of allowing the chemical affinities of substances to depend upon their electrical energies is very piquant; a host of chemical phenomena, as well as conditions modifying them, can be expressed thereby. . . . However, if this idea be examined very carefully one finds it without a sufficiently solid basis."[2]

But Davy had a forerunner. Grotthuss in 1805 closed his famous communication concerning the first theory of the electrolytic dissociation of water, with these words: "Nature can neither create, nor destroy, since the quantity of matter can neither be increased nor decreased; on the

[1] Ostwald's *Klassiker*, No. 45, p. 35ff.
[2] Gilb. Ann., 28, 321 (1808).

contrary all substances may be subjected to a mutual interchange of elements. If one considers the wonderful workings of electricity, active sometimes in secret, even though distributed universally, it is not difficult to see it as one of the most effectual forces in the accomplishments of nature."

The principle of substitution, the ability to mutually interchange elements in substances, is emphasized here by Grotthuss. Likewise he assumes that all chemical processes require the agency of electricity. Another important view is the following: In 1819 Grotthuss expressed the opinion that "metals are most probably not really simple but that they contain either +E or −E in chemical combination. . . . Since metals are differentiated from one another chiefly by their differing combustibility, which may possibly be the cause of their chemical variations, and since the differences in combustibility are dependent upon the amount of −E bound with the substance, it may logically be concluded that −E alone determines the differences between metals. . . . In any case I consider it as certain that all metals contain −E chemically bound. . . . Negative electricity, that is −E, can again represent the long forgotten phlogiston of Stahl."[1]

These views, expressed one hundred years ago, have the character of a scientific presentiment:—"all metals contain −E chemically bound!" In our day we say:—all metals contain electrons (or −E) in their shells, and the outer electrons determine the chemical character of the given metal.

"Die Elektrizitäten sind im allgemeinen das Primum movens aller chemischen Tätigkeit" (The electricities are in general the prime mover in all chemical activity).[2] With these words Berzelius sums up electrochemical knowledge in 1827, just a century ago, a remarkable prediction of future development. Let us hear his views at several stages of his career. One can summarize these views in the form of six statements.

[1] Ostwald's *Klassiker*, No. 152, p. 12, 161, 171 f.
[2] Berzelius, *Lehrbuch*, III, pt. 1, p. 144 (1827).

I. "Electricity, which must obey the same laws as ponderable matter with reference to the proportions in which it combines with other bodies, never is liberated in these decompositions. Its chemical influence has therefore escaped the attention of naturalists up to the present time."[1] This assertion of Berzelius, in the year 1811, is indeed remarkable: electricity, being considered as analogous to matter and governed by the same laws of definite proportions (equivalents), appears here in an atomic state and combines with material atoms.

II. "The body of facts which we already possess concerning electricity as a chemical agent, hardly permits us to think of a chemical process that is not also electrical. Thanks to Davy's brilliant work we have found that two bodies which show a relationship to one another . . . always exhibit opposite electricities when they are about to combine, this fact being more pronounced the greater the mutual relationship. This reveals the possibility of expressing the electrochemical behavior of substances in numerical values."[2]

III. In 1811 Berzelius published an article[3] entitled "Attempts at a Latin nomenclature on the basis of electrochemical behavior." In it he says: "Two bodies, which are about to enter into chemical combination, develop opposing electricities which increase as the moment of such combination is approaching. As soon as combination has taken place an equilibrium is set up, and, dependent upon the difference in the intensity of the chemical action, heat or even flame is produced."

IV. Concerning organic compounds he says: "The chief condition in organic synthesis seems to be an electrochemical modification in the elements, which differs from that which they originally possessed in inorganic nature." Today we say the organic compounds are "homeopolar."

V. Further:—"The electrochemical discoveries of the last decade have probably not deceived us in showing that chemical affinities are dependent upon the electrochemical

[1] Gilb. Ann. der Physik, **38**, 194 (1811).
[2] Ibidem, p. 189 ff.
[3] J. de Phys., 1811, October; *see also* Gilb. Ann. d. Physik, **42**, 37, 282 (1812).

properties of the substances, and are more pronounced the greater the electrochemical contrast of the bodies entering into combination. . . . Experience teaches us that substances of but slight electrochemical difference, that is, where the relationships are weak, can be made to combine only at low temperatures. At higher temperatures they are decomposed. . . . Experience demonstrates that an electrical polarization takes place on contact between two substances of contrasting electrochemical properties. This increases when the temperature is approached at which these opposing tendencies became active. This polarization then disappears, with resultant combination and appearance of flame."[1]

VI. In 1818 Berzelius announced his famous and much disputed dualistic electrochemical theory. In the first place every atom is—as one would express it in our day—a "di-pole," that is, it contains both kinds of electricity in separate places. The absolute quantities of the latter may vary, such that the chemical affinity of an atom is dependent upon the size of the electrical charge. Sodium chloride is therefore formed by the electrostatic attraction of positively charged sodium atoms and negatively charged chlorine atoms. (The fact that negatively charged chlorine could replace positive hydrogen in organic compounds, gave rise to a point of attack against the dualistic theory.)

A summary of these theories clearly gives one the impression that the chemist of one hundred years ago stood closer to our present-day electronic teachings than did the chemist of twenty-five years ago.

From the "electrogenium" of Gren to our modern "electrons," from the statement by Berzelius that definite proportions of electricity combine with elements,[2] to our present-day theories of electric atoms or electrons, from the dualistic valence theory of the same Berzelius to our views on heteropolar and homeopolar compounds—how widely separated in time are these theories, and yet how closely related!

[1] Berzelius, Gilb. Ann., **50**, 366, 377 (1815).

[2] Ampère, in J. de Phys., **93**, 450 (1821), expressed a similar opinion that atoms of simple bodies contain in chemical combination an unchangeable quantity of free positive and negative electricity which belongs to their constitution.

Kossel, in 1920, said of the theory of Berzelius "that the time has come when, on the basis of the most recent physical observations on the structure of the atom, this theory of the electric nature of chemical valency should be restored to its right."[1]

The substitution of positive hydrogen by negative chlorine (Dumas's metathesis) has recently been explained satisfactorily by Nernst and Moers, who showed that in the electrolysis of lithium hydride, the hydrogen goes to the anode.[2]

Let us bring up two more points of view on problems which may be considered today as actual, and which further illustrate the spiritual connection between the Past and Present of scientific development.

"If we should ask ourselves, 'What is the greatest problem in chemistry?' we should without doubt have to answer 'The decomposition and composition of metals' for these are the basis of all our chemical elements. Without a knowledge of these facts in their minutest detail one will never be able to differentiate positively between the remaining substances." This very modern point of view was expressed in 1812 by Oersted,[3] a fellow countryman of Niels Bohr, and his predecessor in the University of Copenhagen.

Another and yet more modern-sounding view was published in 1851 by the great philosopher Arthur Schopenhauer, who wrote as follows: "In addition, I think that all metals are combinations of two primal substances, still unknown to us. The differences between the metals and their electrical characteristics depend upon the relative quantities of the two primal substances. . . . If one could break up the metals into these components, one would probably also be able to make them. But this door is bolted."[4]

[1] Z. Elektrochem., **26**, 314 (1920).
[2] Z. Elektrochem., **26**, 323 (1920).
[3] Oersted, *Ansicht der chemischen Naturgesetze*, p. 289 (Berlin, 1812).
[4] Schopenhauer, "Parerga und Paralipomena," *Sämtliche Werke*, V, p. 116.

CHAPTER IV

What is an Electrolyte?

> "Eigentümliche Verhältnisse, welche uns eben so unbekannt sind, wie das Wesen der Elektrizität und des chemischen Prozesses, werden in der Konstitution der Elektrolyte obwalten und den übrigen Verbindungen fehlen." (Peculiar relationships, which are still as unknown to us as the nature of electricity and of chemical processes, will prevail in the constitution of electrolytes and will be lacking in other compounds.)
> —Hittorf, 1859.

Genesis of the name and concept "Electrolyte".—Faraday.

THE scientific work, i.e., the experimental and theorectical investigations of the triumvirate Faraday, Daniell, Hittorf represent the corner-stone or more than this, the broad foundation of electrochemical and electronic theories and research down to the present time.

It was Michael Faraday (1791-1867) who in the 7th series of his classical investigations in 1834[1] created the terms: electrode, anode (i.e. "that surface at which the electric current enters"), cathode (i.e. "the positive extremity," "the surface at which the current leaves the decomposing body"), electrolytes, ions, anions (i.e. "such bodies which go to the anode"), cations (bodies passing to the cathode). Let me quote in some detail the original definitions and considerations of this eminent scientist. It is my aim to show the primary conceptions of Faraday himself and to compare them with the developed views of a later period. Likewise I wish to call special attention

[1] Trans. Roy. Soc. London, 1834.

to some ideas of this great philosopher which remained in a latent state during many decades or were entirely overlooked. Only a new phase of physical chemistry has developed many kinds of theoretical views akin to those old, disregarded thoughts of Faraday.

Faraday says: "Many bodies are decomposed directly by the electric current, their elements being set free. These I propose to call *electrolytes*. Water therefore is an electrolyte. Those bodies which, like nitric or sulphuric acids, are decomposed in a secondary manner are not included under this term. . . . The term electrolytical will be understood at once: muriatic (i.e. hydrochloric) acid is electrolytical, boracic acid is not.

"It is evident that all the cases in which decomposition does not occur may depend upon the want of conduction. . . . Decomposition depends upon conduction and not the latter upon the former." Further, "in the various electrolytes . . . decomposition and the transmission of a current are so intimately connected, that one can not happen without the other." Then, "upon the whole it appears probable that all those binary compounds of elementary bodies, which are capable of being electrolyzed when fluid, but not while solid, according to the law of liquido-conduction, consist of single proportionals of their elementary principles.

"A body decomposable directly by the electric current, i.e., an electrolyte, must consist of two ions, and must also render them up during the act of decomposition.

"There is but one electrolyte of the same two ions.

"Compound ions are not necessarily composed of electrochemical equivalents of simple ions. For instance, sulphuric acid, boracic acid, phosphoric acid, are ions, but not electrolytes, i.e., not composed of electrochemical equivalents of simple ions." (Let us remember that acids were regarded at that time as anhydrides in the sense of Lavoisier and Berzelius—such as SO_3, P_2O_5, etc.)[1]

[1] Michael Faraday, *Experimental Researches in Electricity*, I, (London, 1839).

These quotations may be summarized as follows. Substances which in the liquid state conduct the electrical current, and only those, are decomposed by the current. Electrolytes are substances which, in the liquid condition, conduct the electric current, and which are broken up directly into their component elements by the current. With reference to their *chemical composition*, electrolytes are binary compounds of elementary atoms corresponding to their chemical equivalents. With reference to their *chemical character*, electrolytes may be acids (hydro-acids, such as HCl), or salts of these acids (such as NaCl, PbCl), or metallic oxides (HO = water, PbO).

Since only compounds with equal numbers of atoms or with "single proportionals of their elementary principles" are decomposable, only the simple binary compounds are originally included in the special class of electrolytes. At the same time Faraday emphasizes the fact that when two elements are capable of combining in multiples, only the lower members are decomposable and conduct the electric current. Thus the lower chloride and iodide of tin (i.e. $SnCl_2$ and SnI_2 or in Faraday's notation SnCl and SnI) readily conduct and are decomposed, whereas stannic chloride and iodide neither conduct nor are decomposed.

Modern theorists have worked up this fact. A. Werner[1] emphasizes these "differences in the case of compounds where there are lower and higher stages of halogenation. The lower ones are solid and salt-like, whereas the higher ones are often liquid, resembling the metalloid halides." W. Biltz[2] has recently taken up this subject, and has found that the melting point may be employed as a new means of differentiation. Biltz deduces the following law: "If an element forms various chlorine compounds, the one with the lower melting point is a poorer conductor, in the fluid condition, than the one with the higher melting point."

According to Faraday the following substances occur in ionic form:

[1] *Neuere Anschauungen . . .*, p. 98 (4th ed., 1920).
[2] Z. physik. Chem., 100, 59 ff. (1922).

Cations: Hydrogen (= 1), potassium (= 39.2) and potassa (= 47.2 = KO where O = 8), sodium (Na = 23.3) and caustic soda (= NaO = 31.3), ammonia (= NH_3 = 17), barium (= 68.7) and baryta (BaO = 76.7), magnesium (= 12.7) and magnesia (= 20.7), "protoxides generally," quinia (= 171.6), cinchona (= 160), and others.

Anions: Oxygen (= 8), chlorine (=35.5), bromine (= 78.3), iodine (= 126), fluorine (= 18.7), cyanogen (= 26), sulphuric acid (= SO_3 = 40), selenic acid (= SeO_3 = 64), nitric acid (= NO_5 = 54), carbonic acid (= 22 = CO_2), acetic acid (= 51, $(CH_3CO)_2O$ = 54), sulphur (= 16), and others.

Briefly, it may be said that elemental bodies and also acid anhydrides and metallic oxides occur as ions. Accordingly, salts are made up in two ways: first, salts of hydro-acids such as sodium chloride and barium chloride; secondly, salts of oxy-acids and oxides, such as $NaO{\cdot}SO_3$, $KO{\cdot}NO_5$, or $CuO{\cdot}SO_3$, etc.

It seems to me that Faraday intended the word "electrolyte" to have a signification different from that which electrochemists now give it. "Electrolytes" should be decomposed into "their elements"; that is, the term "electrolyte" was meant to include only those simple binary substances composed of elementary atoms, which could be decomposed into elementary atoms, not radicals, by the electric current. If we compare our present day concept of a "true salt," especially with regard to its *crystalline*, ionic, structure, as opposed to "pseudo-salt", with the above meaning of electrolyte as propounded nearly a hundred years ago, and if we examine the composition of those substances which correspond to the term "true salt," it will quickly become apparent that in general the class of "true salts" of today, especially in their formulation by means of equivalent weights, contains the same bodies as the electrolytes of Faraday—simply constructed and composed of elementary atoms (halides, oxides, sulphides, etc., of the alkali and alkaline earth metals).

Let me emphasize still a few more concepts of Faraday, views which became important in the views of his suc-

cessors. In 1833 Faraday wrote: "An analogy in condition exists between the parts of a body in solution, and those of a body in vaporous or gaseous state."[1] It is a curious fact, that the same analogy, fifty years later, was used by van't Hoff who obtained the laws of this analogy by his osmotic theory of solution (1884–1887).

Further: "We have but very imperfect notions of the real and intimate conditions of the particles of a body existing in the solid, the liquid and the gaseous state; but when we speak of the gaseous state as being due to the mutual repulsions of the particles or of their atmospheres, although we may err in imagining each particle to be a nucleus to an atmosphere of heat or electricity or any other agent, we are still not likely to be in error in considering the elasticity as dependent on mutuality of action." There is surely close similarity between our present-day atomic models with the small nucleus of protons and electrons and the outer shells of electrons, and this model of Faraday's.

In formulating a theory of the action of the electric current on a liquid conductor, Faraday wrote in 1833: "The theory which I have ventured to put forth (almost) requires the conclusion, that in a compound body capable of electro-chemical decomposition the elementary particles have a mutual relation to, and influence upon each other, extending beyond those with which they are immediately combined. Thus in water, a particle of hydrogen in combination with oxygen is considered as not altogether indifferent to other particles of oxygen, although they are combined with other particles of hydrogen; but to have an affinity or attraction towards them, which, though it does not at all approach in force, under ordinary circumstances, to that by which it is combined with its own particle, can, under the electric influence, exerted in a definite direction, be made made even to surpass it. . . This general relation of particles already in combination to other particles with which they are not combined, is

[1] *Experimental Investigations*, VI, §657 (1833).

sufficiently distinct in numerous results of a purely chemical character; especially in those where partial *decompositions* only take place . . . and it probably has a direct relation to, and connection with, *attraction of aggregation*, both in solids and fluids. It is a remarkable circumstance, that in gases and vapors, when the attraction of aggregation ceases, there likewise the decomposing powers of electricity apparently cease. . . . It seems not unlikely, that the inability to suffer decomposition in these cases may be dependent upon the absence of that mutual attractive relation of the particles, which is the cause of aggregation."[1]

The reading of these old words brings to life a whole series of modern views. It recalls the "secondary" and "partial valences" of present-day chemistry. Do we not give to substances, despite the fact that they are saturated and combined, for example to molecules of water H_2O, remaining "amounts of affinity" or "secondary" valences, which may exercise an influence upon other molecules or upon their own kind? Do we not link *association* and the formation of associated molecules such as $(H_2O)_x$ with the influence of these secondary valences? Is not the phenomenon of association, the tendency to the formation of complexes, ionization, etc., charactertistic of polar bodies?[2] G. N. Lewis[3] regards the association of such strong ionizing agents as H_2O and HCN as due to the presence of lone electron pairs, that is free electrons. W. Kossel[4] believes the formation of autocomplexes and complexes in general to be due to an electrostatic attraction which an ion exercises "not only toward certain particular ones by virtue of valence relationships, but also toward all others" which are oppositely charged.

[1] Op. cit., §523 (1833).
[2] G. N. Lewis, J. Am. Chem. Soc., 38, 763 (1916).
[3] *Valence and the Structure of Atoms and Molecules*, p. 109 (1923).
[4] Z. Elektrochem., 26, 317 (1920).

CHAPTER V

Daniell's Researches. New Kinds of Ions; Constitution of Electrolytes

FOLLOWING the pioneer work of Faraday came a series of investigations more replete in chemical detail, by his countryman, Daniell, in 1839. He was the first to determine accurately the constitution of ions, and he did much to increase the fund of knowledge concerning the ions of salts.[1] In interpreting these questions from the chemical standpoint he showed himself to be not only superior to Faraday, but far ahead of his time.

On the basis of his experimental work he came to the conclusion that the chemical formulas of electrolytes which had heretofore been accepted, were in need of revision if ions were to be regarded as components of salts. Thus, for the earlier chemical expressions, he substituted the following electrolytic formulas:

	chemical formula	electrolytic formula
sodium sulphate	$(S + 3O) + (Na + O)$	$(S + 4O) + Na$
potassium sulphate	$(S + 3O) + (K + O)$	$(S + 4O) + K$
potassium nitrate	$(N + 5O) + (K + O)$	$(N + 6O) + K$
copper sulphate	$(S + 3O) + (Cu + O)$	$(S + 4O) + Cu(=31.6)$
sal ammoniac	$(Cl + H) + (N + 3H)$	$Cl + (N + 4H)$
ammonium sulphate	$(S + 3O) + (N + 3H)$	$(S + 4O) + (N + 4H)$

(The atomic weights in Daniell's notations are the same as in Hittorf's work).

[1] Trans. Roy. Soc. London, 129, 97 (1839); 130, 209 (1840).

Salts are no longer to be regarded as compounds of acids and bases, that is, of acid anhydrides and metallic oxides, but of metallic cations and elemental or compound acid anions. The difference between hydro-and oxy-acids disappears, since we have directly comparable objects and relations, *e.g.* (H + Cl) and (H + SO_4), (Na + Cl) and (Na + SO_4).

The sequence and mutual influence of ideas, which were far apart in time and belonged objectively to different problems and fields of scientific endeavor, are presented in a comprehensible manner by these results of Daniell's investigations. Daniell refers to Davy and Berzelius in support of his views concerning the constitution of salts. The theory of Davy, as developed by Liebig, stated that radicals such as chlorine, cyanogen, and sulphate (SO_4) formed acids with hydrogen and salts with metals. Although an opponent of this theory, Berzelius in 1825 regarded sal ammoniac as the chloride of a hypothetical, metal-like radical, ammonium (NH_4). In the field of organic chemistry Liebig (1838) had demonstrated the correctness of the view that acids are hydrogen compounds, i.e. binary combinations of hydrogen and a complex organic radical. The facts which served to unify this whole series of divergent ideas were found by Daniel (1839) in his electrolytic results. These in turn had a beneficial effect upon the fate of Liebig's acid theory and helped to further investigations concerning the constitution of organic acids.

Together with W. A. Miller, Daniell investigated a large number of dissolved salts of various types, made experiments with "transference," determined the nature of ions, in short, did very much to expand knowledge in the field of the kinds and structure of electrolytes.[1]

Electrolytes are divided as follows:

1. "Simple electrolytes," where the electrolyte is composed of simple ions in the same number, as K, I; Ag, Cl.

2. "Complex electrolytes" composed of a compound cation and a simple anion, such as NH_4,Cl.

[1] Trans. Roy. Soc. London, 134, 1 (1844).

3. "Complex electrolytes" made up of a simple cation and a compound anion, as K, SO_4; Na, NO_6.

4. Those consisting of compound anions and cations, such as NH_4, SO_4.

These four classes are considered collectively under the name of "monobasic electrolytes" (mono-mono-ionic salts).

5. The final class, includes electrolytes which contain two or more equivalents of cations and a compound anion, such as K_2, $FeCy_3$ (now known as $K_4Fe(CN)_6$), and Na_3, P_2O_5, O_3. These are the "polybasic electrolytes."

By this classification Faraday's narrow definition of electrolytes is put aside. Electrolytes include salts of all types and various compositions. Generally speaking, all salts, acids, and bases, which conduct the electric current and are decomposed by it, are to be regarded as electrolytes.

However, Daniell observed many other interesting facts and made mention of them. He placed potassium ferrocyanide in class 5, a salt which was put into the category of complex salts by Ostwald in 1889. It is indeed deserving of mention that Daniell and Miller observed the potassium of the salt to go to the one pole and the whole ferrocyanide complex to go to the other. On the basis of their observations the composition of the salt could only be $4K^+$ (as cation) and $Fe(CN)_6^{=\,=}$ as anion, in analogy with potassium sulphate = $K^+ + SO_4^-$. It seems that these facts logically demonstrate the formula $K_2Fe(CN)_3$ now written $K_4Fe(CN)_6$. But nevertheless for half a century following Daniell's investigations this substance was considered as a double salt of a molecular combination $4KCN + Fe(CN)_2$. One may ask: How could such an erroneous formula exist so long? The explanation may be, first, that experimental chemists took no cognizance of the theories of the electrochemists; and, second, that for experimental chemistry the old valence theory (that iron could be only bivalent or trivalent) was the fundamental rule.

But still another detail did not escape Daniell's observation. He reasoned that if potassium sulphate and sul-

phuric acid possessed the formulas $K + SO_4$, and $H + SO_4$ respectively, one might expect electrolysis to isolate the compound anion SO_4 as a *free radical*. He electrolyzed sulphuric acid at $-20°C$ and determined that much less oxygen is evolved than would be expected from the hydrogen obtained. Consequently he assumed the presence of the radical $S + 7O$, but could not isolate it in the free state. Only many decades later, using highly refined experimental methods, did Marshall (1891) succeed in preparing by electrolysis, per-sulphuric acid, $H_2S_2O_8$, or Constam and Hansen (1896) per-carbonic acid, $H_2C_2O_6$ and Fichter, (1918) per-phosphoric acids, $H_4P_2O_8$ and H_3PO_5.

The question of the nomenclature of ions also occupied Daniell's attention. What are the compound residues of sulphuric and nitric acids that "wander to the zincode," to be called? Daniell proposes the names "oxy-sulfion" and "oxy-nitrion," the former composed of $S + 4O$, the latter of $N + 6O$. Copper sulphate is, accordingly, "oxy-sulfion of copper," while potassium nitrate is potassium oxy-nitrion. Can this problem be considered as solved today? Or must we say that the question of a short and definite terminology of ions requires attention and solution, expecially at this time? We use the term "nitrate" for totally different things, when we say "ethyl nitrate," $C_2H_5NO_3$, and "potassium nitrate." And when we write and say "potassium nitrate," KNO_3, does this express our ideas of the condition of the salt in solid form (in its ionic lattice) and in solution (as totally dissociated into ions)? Is not this name a left-over from the time and theories of a century ago? The old term "potassium oxynitrion," which took into account the ionic state, seems to me to correspond more closely to our modern views than the term "potassium nitrate" of our days.

Long ago chemists discussed the question of a rational, international, nomenclature for the compound substances of organic chemistry; such a nomenclature has been established. Would it not be in conformity with the international spirit of chemistry and the great progress of

the special branches of this science, to revise and rationalize all chemical nomenclature in agreement with modern scientific views?

"*All Electrolytes are Salts*" (Hittorf, 1859).

The investigations of Hittorf may be regarded as a continuation of those of Daniell, but much more elaborate and quantitative than those of the latter. Questions of constitution were the order of the day. New classes of compounds, both inorganic and organic, were being brought to light. Measurements of chemical affinity involving both organic and inorganic substances were being made by various workers.[1] Williamson had published his interesting and important dissociation theory[2] in 1851. Thermochemistry had been founded.[3] Relationships between chemical and electrical energy had been advanced for discussion.[4] Into this high-tension scientific atmosphere comes Hittorf (1824-1914) with his classical researches "Concerning the Movement of Ions during Electrolysis" (1853-1859), in which he sheds new light upon the character and chemical nature of electrolytes and non-electrolytes. On the basis of his very exact transference measurements of various substances in aqueous solution, he reaches in 1859 the following general conclusions concerning the nature of electrolytes.

"All electrolytes are salts[5] in the light of our newer chemistry. During the course of electrolysis the same sort of an exchange takes place between similar components of molecules as in the case of double decomposition. This exchange aids in that movement of the molecules, which we call an electric current."[6] This exchange (in such chemical reactions) is lacking in the case of those com-

[1] Rose, 1851; Bunsen 1853; Gladstone 1855.

[2] Ann., **77**, 45 (1851). Compare Faraday's views on interatomic action between different molecules.

[3] Hess, 1840; Favre and Silbermann, 1852; Julius Thomsen, 1851.

[4] Helmholtz, 1847; William Thomson, 1857.

[5] Because Hittorf considers as "electrolytes" salts, acids and bases (basic oxides) it is evident that in his definition, all electrolytes are salts.

[6] Ann. Physik, **106**, 572 et al. (1859); Ostwald's *Klassiker*, Nos. 21 and 23.

pound bodies which do not conduct the current at all or only under certain particular circumstances. "All compound substances which are good conductors of electricity, mutually exchange their ions when they come into contact with each other in liquid condition" because "the decomposability is proportional to the electrical conductivity." With regard to "salts" the same view was expressed by Hittorf some years later. In rejecting the conception of many chemists who supposed that the chemical process is a kind of "attraction phenomenon" (Newton) he said: "Längst waren vorurteilsfreie Chemiker, wie Gay-Lussac, Williamson, zur Einsicht gekommen, dass dieser Austausch der Salze nicht als Wahlverwandtschaft gedacht werden kann, sondern dass Salze diejenigen chemischen Verbindungen sind, welche ununterbrochen ihre Bestandteile gegeneinander austauschen, und dadurch von den anderen Verbindungen welche zur Zersetzung noch bessere Bedingungen bedürfen unterscheiden."[1]

A host of new facts and ideas are brought close to us by this theory of Hittorf's. The chemical reactivity of salts is linked fundamentally with electrical conductivity. In electrolysis, in conduction, and in chemical metathesis, ions are regarded as the universal and necessary things. It is of great scientific charm to look backwards and recall to mind the distinct steps in the development of this theory. First Grotthuss, Davy, and Berzelius express the view that chemical affinity and electrical forces are probably of the same kind or identical, and they expect that future investigations will develop a method for measuring these forces. Then Faraday demonstrates that salts (in solution or liquid state) are easily decomposed by the electrical current if they are conductors of the current. Next comes Williamson (1851) who rejects the theory of the chemists:—atoms in a molecule are not in a state of

[1] Wied. Ann. d. Physik, **4**, 374 (1878). Openminded chemists like Gay-Lussac and Williamson had long ago arrived at the opinion that this exchange of salts could not be thought of as an elective affinity, but that salts were chemical compounds which continually exchange their components with one another. In this way they can be differentiated from other substances which require more favorable conditions for decomposition.

repose, but in a perpetual exchange! The physicist Clausius (1857) however imposes a restriction, admitting such an exchange in sporadic cases only. Yet Hittorf concludes (1858) that Faraday's law, which has credit for the weakest electrical currents, stands in contradiction to the chemical views on the state of a liquid compound substance: "the ions of an electrolyte cannot be combined in a stable form to whole molecules and these cannot exist in a definite regular arrangement."[1] A new and revolutionary view is entering into chemistry! The salt molecules or particles which during many centuries were considered as stable in fire and water, are thought to be decomposed in water solution or to be spontaneously decomposed into free ions! As a measure of such a decomposition and likewise of a chemical activity, should be considered the electrical conductivity! Indeed, an uncommon and unexpected view, quite contradictory to the views of that period of chemical knowledge, and therefore without effect on his contemporaries. The self-acting, mental "brake" came promptly into action, *i.e.* a storm of opposite views, refutations, controversies, etc., was the next visible result, which had the further consequence that they diverted Hittorf from these investigations. He turned aside from these problems, and the keys to an electrolytic dissociation theory slipped from his hands. It is clearly to be seen that these researches really laid the foundation for the electrolytic dissociation theory of Svante Arrhenius (1887) and for the further advances by Bjerrum, Milner, Ghosh, Debye, and others in the 20th century.

For the characterization of "electrolytes," "salts" as individuals, further quotations may be made from Hittorf's works.

"The so-called basic oxides may serve as type-electrolytes, to which we may give the formula MO. . . . The non-basic oxides are not electrolytes." Substitutions can be made for either the anion or cation in the type substance MO, containing the ions M and O.

[1] See Ann. Physik, 103, 54 (1858).

1. SUBSTITUTION OF THE ANION IN *MO*

The following electrolytes may be obtained by replacing the anion.

(a) MO: M/(SO_3+O); M/(NO_5+O); M/Cl; M/Cy; M/S. Oxides, sulphur, cyan and halogen compounds can combine among each other, thus

(b) K/(CyAg+Cy); Na/($PtCl_2$+Cl); K/(Au_2Cl_3+Cl);

$$K/(ClHg + Cl);\ K/\left(\frac{FeCy}{2} + Cy\right).^{1}$$

Hittorf argues that "these results break down the points of difference between the compounds of oxides and chlorides"; that is, the salts of the oxy-acids are of the same type as those of the hydracids. We meet anew the problem: oxygen- or hydrogen-acid theory. We are familiar with the views of Lavoisier and Davy, Berzelius and Liebig, learned the arguments of Daniell and came to know Hittorf's conclusions. This list of famous names demonstrates the scientific importance of the acid-question, and the relationship between the different branches of chemical research and the different periods of chemistry. Further, Hittorf noted that the so-called double salts behave during electrolysis in such a manner that only the alkali metal acts as a cation, whereas the metal-containing residue as a whole forms the anion. (Compare this with the results of Daniell's researches).

(c) Halogen compounds may combine among themselves to form associated or polymerized molecules, and be electrolyzed into double salts like the compounds under (b):

$$Cd/(CdI + I),\ Zn/(ZnCl + Cl),\ Zn/(ZnI + I).$$

This was a new and important advance in the development of our problem "salts-acids-bases." First, a new view as to the state of dissolved salts was proposed, *i.e.* a salt

[1] The atomic weights of Hittorf were: O = 8; S = 16; Cu = 31.5; N = 14; H = 1; C = 6; Pb = 103.8; Cl = 35.4; I = 126; K = 39.2; Na = 23.2; Zn = 32.2; Cd = 55.8; Hg = 101.4; Ag = 108.1; Fe = 27.2; etc.

exists not only in single molecules, but forms also molecule-aggregations, associated molecules or auto-complexes. Thus, cadmium iodide can exist as CdI_2, $(CdI_2)_2$, $(CdI_2)_3$. It was Faraday who developed the view of such "attractions of aggregations" between molecules of the same kind, but it was Hittorf who made the first application concerning electrolyte molecules. Second, a new experimental method (by transference numbers) was devised for the demonstration of such molecule aggregations. Third, a new form of electrolytic dissociation, *i.e.* of stepwise decomposition in special complex ions, was introduced into electrochemistry. As, for example,

$$(CdI_2)_2 \rightarrow Cd^{++} + CdI_4^{--} \rightarrow Cd^{++} + CdI_3^{-} + I^{-}$$

Fourth, by using alcohols instead of water as solvent, Hittorf found an increased tendency toward the formation of complexes, *i.e.* non-aqueous solvents have a different action on salt molecules, and that an electrical decomposition or ion-formation, but of another kind, takes place also in non-aqueous solvents. Hittorf gives the following (old) formulas (cadmium iodide = CdI, where Cd = 55.8):

$$(CdI)_3 \rightarrow Cd^{+} + (2CdI + I^{-}),$$

or

$$(CdI)_4 \rightarrow Cd^{+} + (3CdI + I^{-}), \text{ etc.}$$

That is, complexes exist here containing three, sometimes four "atoms" (molecules) of the salt. "Iodine goes to the anode along with two or three undecomposed salt molecules." By decreasing the concentration the complexity of molecules and ions have been decreased. It may be added that the idea of auto-association (auto-complex formation) of molecules and ions became one of the fundamental points in theoretical views of electrochemistry up to our day. (We shall later return to this question). Let us continue the examination of Hittorf's work.

II. SUBSTITUTION OF THE CATION IN TYPE-COMPOUND *MO*

If hydrogen takes the place of a metal, water is formed. "Water is on the border line of electrolytes and stands as a

transition compound to non-conducting oxides." However, many hydrogen compounds are exceptional electrolytes, or conductors, such as

$$ClH,\ (SO_3+O)H,\ IH,\ BrH,\ (NO_5+O)H.$$

Replacement of hydrogen in these substances by such alcohol radicals as methyl, ethyl, amyl, results in the formation of non-conductors. Hydrogen may also combine with certain substances and yield metal-like cations, such as

$$H + NH_3 = NH_4,\ Cl(H + NH_3),\ Cl(H + \text{alkaloid}).$$

In the case of the organic bases ("alkaloids") a halogen, oxygen or cyanogen group may be introduced in place of the hydrogen with no effect upon the "basic character" of the radical. The residue containing chlorine, oxygen, etc., goes to the cathode. The hydrogen atoms of ammonium, NH_4, may be replaced by alcohol radicals resulting in the formation of electrolytes, such as tetra-ethyl ammonium oxide, which in their behavior simulate aqueous solutions of caustic potash. The rôle of the nitrogen in these compounds may also be assumed by phosphorus, arsenic, and antimony (*i.e.* phosphonium, arsonium, and stibonium bases).

Frankland and Löwig even combined basic metals and alcohol radicals into metallo-organic compounds. "Such compounds, acting like ordinary salts, are also to be considered electrolytes." Further: "The uranyl cation of Peligot (U_2O_2 in the salt $(U_2O_2)Cl$) is the most remarkable, and also most markedly in contradiction to accepted theories, since it discharges at the cathode."

"I shall conclude, with its mention, the summary of various chemical compounds which have become known to me as electrolytes. Very few compound ions are capable of existence in the free state. When discharged upon electrolysis, most of them decompose in that their elements combine in a different manner."[1]

[1] Ann. Physik, 106, 560 et al. (1859). Compare the above statements with those made by Daniell.

We have purposely chosen the inclusive, literal quotations from Hittorf's conclusions for two reasons: first, because of the clear manner in which he has expressed his ideas, and secondly, to call again to mind the wealth of suggestions and problems which were advanced by him. It is indeed worth while to note how much time was required for new researches to transform the above problems into the proven tenets of modern chemistry. It is really amusing to observe that whereas a single chemist can carry out a chemical reaction and thereby obtain the proof of a new idea in some days or weeks, a multitude of chemists apparently needs some years or even decades, for their mental reaction, before they approve, recognize and assimilate this same new idea!

The problem of the so-called "double salts" was satisfactorily cleared up by W. Ostwald.[1] If a "double salt" salt shows an anomalous behavior in aqueous solution, it is a "complex salt" or the salt of a "complex acid."[2] The problem of complex salts and electrical conductivity was brilliantly attacked from a new direction by Werner. The result was his co-ordination theory of metal ammonias, the stereochemistry of inorganic salts, *i.e.* a new kind of inorganic chemistry.

The phenomenon of auto-formation of complexes in the case of salts and of stepwise dissociation, was explained by the investigations of Loeb and Nernst (1888) on silver salts, W. Ostwald (1889) on acids, Bredig (1894) on magnesium salts, etc.[3] That this problem as a "pièce de resistance" continues to be a dominant question in the newest phase of the electrolytic dissociation theory, can be learned from the investigations of Bjerrum, and from the recent discussions at the meeting of the Faraday Society (April 1927): "most of the electrolytes are associated to a greater or less extent" (Onsager), or "sodium, potassium and silver nitrates, however, must be partially associated" (McInnes).

[1] Z. physik. Chem., **3**, 596 (1889).
[2] See Abegg and Bodländer, Z. anorg. Chem., **20**, 453 (1899).
[3] Walden, *Leitvermögen*, I, p. 157 ff. (1924).

The salts of the alkylated ammonium, phosphonium, arsonium, stibonium, sulfonium, and telluronium bases were first studied thoroughly with reference to their electrolytic nature by G. Bredig.[1] The investigations of Dietrich[2] and Ley[3] furnished the first observational material concerning the salts of the uranyl cation $U_xO_2^{++}$ (in the salts like $UO_2(NO_3)_2$, $UO_2 \cdot Cl_2$, $UO_2(CH_3COO)_2$, or $UO_2 \cdot SO_4$ etc.) which had been particularly emphasized by Hittorf.

The halogen alkyls and halogen aryls, RX, considered by Hittorf as non-conductors, were first investigated by Walden[4] who demonstrated that such salts as triphenyl methyl bromide and especially iodide were good conductors in liquid sulphur dioxide and might therefore be looked upon as carbonium salts, $(R_3C)^+X^-$.[5] The statement of Hittorf with reference to the probable salt-like character of metal alkyls is also remarkable. It took more than a half a century to demonstrate this point experimentally. Schlenk[6] showed that the sodium aryls yielded electrically conducting solutions in ether, but it was particularly Hein[7] who in a conclusive manner proved the electrolytic nature of the metal alkyls and the halogenoid character of the C_2H_5 group in them.[8] Kraus and Rosen offered evidence for the salt-like character of sodium triphenyl-methyl.[9]

Isolation of free radicals.

One of the last problems discussed by Hittorf was the isolation of free radicals or compound ions. He wrote: "Very few compound ions are capable of existence in the free state." This was also the opinion of Daniell (1844).

[1] Z. physik. Chem., **13**, 191, 289 (1894).
[2] Z. physik. Chem., **29**, 449 (1899).
[3] Z. physik. Chem., **30**, 193 (1899).
[4] Ber., **35**, 2020 (1902); Z. physik. Chem., **43**, 454 (1903).
[5] *See also* Gomberg, Ber., **36**, 385 (1903); J. Am. Chem. Soc., **44**, 1818 (1922), and **45**, 206 (1923).
[6] Ber., **47**, 1678 (1916); **50**, 271 (1917).
[7] Z. anorg. Chem., **141**, 161 (1924); **158**, 153 (1926).
[8] Not without interest is the fact that Lowry, in the Trans. Faraday Soc., **19**, Pt. 2, 497 (1921), postulated the heteropolar character of zinc methyl, $Zn^{++}CH_3^-CH_3^-$ on the basis of the electronic theory of valence.
[9] J. Am. Chem. Soc., **47**, 2739 (1925).

And fifty years after Daniell, the same view remained dominant because new facts had not come to light. Even as late as 1895 Wilhelm Ostwald wrote, "Many years passed before it became evident that radicals, by their inherent nature, are incapable of isolation. Only recently have scientists comprehended that they are similar to ions."[1]

Since then, new discoveries have been made. Gomberg in 1900, was the first to isolate the free radical triphenyl methyl, $(C_6H_5)_3C$. The long existant prejudice was broken down, and thanks to the efforts of Gomberg, Schlenk, Wieland, and others, we now know a large group of such free hydrocarbon radicals.[2] Schlenk and Herzenstein[3] showed that the same free radical could be obtained from its state as a cation in the salt-like bromide, $(C_6H_5)_3C^+Br^-$, by electrolysis in liquid sulphur dioxide. In a like manner the free ammonium radicals were obtained by the electrolysis of their halogen salts in liquid ammonia. Among them were tetra-methyl ammonium, $N(CH_3)_4$,[4] tetra-propyl ammonium, $N(C_3H_7)_4$,[5] tetra-ethyl ammonium, $N(C_2H_5)_4$,[6] and also phosphonium, arsonium and other radicals.[7]

The existence of a great number of such triarylmethyl compounds in free form, *i.e.* as $(R)_3C$, according to the equation (and directly determined molecular weights): $(R)_3C{\cdot}C(R)_3 \rightarrow 2(R)_3C$, and the analogy in the chemical behavior between the ammonium, phosphonium, sulfonium, and arsonium radicals and the free (monatomic) alkali metals (potassium or sodium), can be considered as a sufficient support for the view that in all these cases we have indeed free radicals before us, *i.e.* derivatives of a trivalent carbon atom and of tetravalent N, P, As, or trivalent sulphur atom. (Direct measurements of the mole-

[1] *Elektrochemie, Ihre Geschichte und Lehre*, p. 625 (1895).

[2] P. Walden, *Chemie der freien Radikale* (Leipzig, 1924); Gomberg, Chem. Reviews, **1**, 91 (1924); Schlenk, Sitzb. preuss. Akad. Wiss., **31**, 1927.

[3] Ann., **372**, 11 (1910).

[4] McCoy and Moore, J. Am. Chem. Soc., **33**, 273 (1911); McCoy and West, J. Phys. Chem., **16**, 261 (1912).

[5] C. A. Kraus, J. Am. Chem. Soc., **35**, 1732 (1913).

[6] Schlubach, Ber., **53**, 1889 (1920).

[7] Schlubach and Miedel, Ber., **56**, 1892 (1923).

cular weight are needed). The existence of such compound radicals (with an unusual valency) in free (monomolecular) state is therefore demonstrated, both by chemical methods and by electrolytic experiments (isolation of the cation). By the electrolysis of tetraphenyl chromium iodide in liquid ammonia, Hein and Eissner[1] were able to isolate tetraphenyl chromium $[(C_6H_5)_4Cr]_n$ as a complex cation, but in polymeric form. Without doubt the great success in isolating free radicals as *cations* has been a stimulant for the experimental work with regard to free complex *anions*. Indeed, not only the same electrolytic method in application to alcoholic solutions of potassium salts, but also chemical reactions, led to the isolation of a number of compound anions. We may mention the following examples: Thiocyanogen, $(SCN)_2$,[2] oxycyanogen, $(OCN)_2$,[3] seleno-cyanogen, $(SeCN)_2$, and telluro-cyanogen, $(TeCN)_2$, and also the peculiar halogenoid radical, azido-carbondisulphide, $(SCSN_3)_2$, discovered by Browne.[4]

Using the term "free radicals" for these anionic or halogenoid compound radicals, we must differentiate between two things: first, the principal fact that such a kind of radical (for example, thiocyanogen, oxycyanogen, seleno- and telluro-cyanogen, or azido-carbondisulphide) generally can be *set free* or isolated, that is, that these radicals are existent in free or liberated state; and second, their molecular state. The great variety in the dissociation and equilibrium of free triarylmethyls, *i.e.*

$$(R)_3C{\cdot}C(R)_3 \leftrightarrows 2(R)_3C$$

where the amount of dissociation (from left to right) can vary between 5 and 100%, brings into discussion the problem: What is the degree of dissociation in the case of the liberated halogenoid (compound) radicals? Is there here an equilibrium between the dimeric or polymeric and the monomeric form, *e.g.* $(SCN)_n \leftrightarrows nSCN$ as in the case $(NO_2)_2 \leftrightarrows 2NO_2$,

[1] Ber., **59**, 362 (1926).
[2] Kerstein and Hofmann, Ber., **57**, 491 (1924).
[3] Birckenbach and Kellermann, Ber., **58**, 786 (1925).
[4] A. W. Browne and others, J. Am. Chem. Soc., **45**, 2698 ff. (1923).

dependent upon temperature, pressure, solvent and concentration? It seems that the experiments up to the present time, particularly the determination of molecular weight in solutions, give a negative answer, *i.e.* that in liberated state, and in some solutions, the dimeric or polymeric form is predominant. This does not exclude the supposition that nevertheless a small amount of free (monomeric) radicals is always present.

We can suppose that there are at least two steps in the formation of these radicals: first, the formation of the "free radical," like a complex "atom" (compare the origin of an elemental atom in "statu nascendi"), for example:

$$KCl: K^+ + Cl^- \rightarrow K^+ \text{ (separated)} + Cl^- \text{ (separated)},$$
$$KSCN: K^+ + SCN^- \rightarrow K^+ \text{ (separated)} + SCN^- \text{ (separated)};$$

second, the formation of the discharged radical in free state (liberated chemical individual):

$$Cl^- + Cl^- - 2\ominus = Cl + Cl \leftrightarrows Cl_2$$
$$SCN^- + SCN^- - 2\ominus = SCN + SCN \leftrightarrows (SCN)_2$$

The reactions commonly reach an equilibrium; in our case, therefore, we must expect among the products of reaction, independently of the dimeric form, also the primary (or free) radicals. If the velocity of formation for the dimeric product is extremely great, and the reversal reaction of decomposition under the given experimental conditions occurs relatively slowly, it is only then that the amount of the (stable) dimeric product will be so considerable that we practically can neglect the small concentration of the primary products. But it is a question for further experimental work to determine the physical conditions which are favorable to the stability of the primary products.

One may ask—Since we know the possibility of isolation of all these radicals (anions), is it not probably possible to isolate likewise other complex anions which contain one of the metallic elements of the VI group in combination with the CN group, for example $Cr(CN)_6$? Or the complex cyanogen-anions of the metals of

the VIII group, for example $Fe(CN)_6$ or $Pt(CN)_6$ or $PtCl_6$ or $Co(CN)_6$? Another class of such free radicals, cations, might be found among the relatively stable complex salts—"metal ammonias"—of Werner; for example, $[Co(NH_3)_6]\cdot X_3$. If in the case of free triaryl methyls the presence of larger or more complex aryls favored the formation and stability of free radicals, did not then analogous relations act in the case of free negative radicals?

All Substances are Electrolytes (Helmholtz, 1881)

> L'activité électrolytique se confond avec l'activité chimique" (Electrolytic behavior is confused with chemical behavior.)—Sv. ARRHENIUS (1884).

The experimental investigations which I have just mentioned show that new classes of compounds and new varieties of ions may be included with "electrolytes." That much new territory remains to be explored was early emphasized by Helmholtz. In his famous Faraday lecture of 1881, Helmholtz, like Grotthuss, Davy, Berzelius and Faraday, took for his subject the identity of chemical relationship and electricity. He regards, as did Gren, Grotthuss, Berzelius and Ampère, both forms of electricity as material things, "even if they were not of a ponderable nature" and sets up the hypothesis that both $-E$ and $+E$ "are divided into distinct elemental quanta, which behave like atoms of electricity."[1] He subsequently raises the question whether electrolytic conduction is limited only to salt solutions and acids, that is, to those compounds which we recognize as electrolytes. On the basis of measurements of potential difference he comes to the conclusion that all bodies are electrolytes, that all of them conduct to a greater or less degree. Even turpentine, benzene, ether, and similar substances give evidences of electrolytic conduction.

Similar ideas were current at that time. They were advanced independently by various investigators and were the expected results of the scientific trend of thought of

[1] Helmholtz, *Vorträge und Reden*, II, 272 (1896).

this period. Thus Maxwell spoke of the charge of an ion as a "molecule of electricity"! Old ideas and old names reappeared. Electricity was a "material thing"—was not such a view a common one about 1800? Did not the old chemists speak of elemental quantities, of distinct equivalents (or proportions) of electricity in its combination with weighable matter? One could perhaps ask:—Have these old views unconsciously influenced the modern views, or did the modern views arise independently and form new sources of knowledge? We can here recognize the rhythm in the development of human cognition, the periodicity of fundamental ideas in science, and it becomes evident that such a periodical recurrence is not an accidental fact, but is the necessary logical consequence of human intellectual capacity and its limitations.

The time about 1880 is a remarkable period in the development of scientific views and experiments. While the one group of scientists endeavored to extend more and more the boundaries of the classical territory of electrolytes, and to make all substances electrolytes, the others followed the lines of Faraday and Hittorf and investigated from different standpoints the classical aqueous solutions of salts. What is the state of a salt-molecule in water? This question became a problem of the day and a matter of dispute. Hittorf had expressed the view, that "salts are such chemical combinations as exchange their components in an uninterrupted manner" or "which mutually exchange their ions when they come into contact with each other in liquid conditions." Of what nature are these components? Hittorf answered: they are ions. However, Williamson supposes that atoms in a molecule are in a perpetual exchange. One can now ask: Are there experimental data of a more objective character which can support such a view? Or, if we admit such an inter-ionic exchange between the different molecules of a given salt, is this exchange an instantaneous reaction which takes place with an enormous velocity, or does it establish a measurable equilibrium between the liberated ions and those combined to a salt molecule? New experimental facts came

from the side of physico-chemical researches on aqueous salt-solutions. The physical properties of salt-solutions had been proved to obey an additive principle.

Valson (1870) demonstrated, by measurements of capillarity and specific density, that dilute equivalent salt-solutions behaved as if the salt-molecules were decomposed into an acid and a metal "radical," that therefore the radicals may be considered as having been set free. Kohlrausch (1879) discovered the "law of the independent mobility of ions": the molecular conductivity of a binary salt is the sum of the conductivities of both ions. H. de Vries (1883) investigated the "osmotic power" of dilute solutions and established the following fact: "In the case of those salts which have been examined, the isotonic coefficient is equal to the sum of the partial coefficients of all of the components." In the year 1881 a Russian chemist Kajander stated that the reaction velocity of acids on metallic magnesium stands in parallelism to the electrical conductivity of these inorganic and organic acids. Therefore he concludes that the acting acid molecules are "opened."[1] In the year 1882 the well-known Russian physico-chemist Lenz came to the conclusion that since the molecular conductivity of a salt in solution is proportional to the velocity of diffusion, the molecules cannot exist in a stable form, but are separated into ions. The French physico-chemist Raoult, who devised the freezing- and boiling-point methods, summed up the general results of his own investigations, thus (1885): "Most of the physical effects produced by salts upon the water in which they are dissolved, are the sum of the effects produced separately by the electropositive and electronegative radicals of which they are constituted, and which act as if they were simply mixed in the liquid."[2]

The electronegative and electropositive radicals of a salt (today we would say, the anions and cations of a salt molecule) act as if they had been simply mixed in the

[1] J. Russ. Phys. Chem. Soc., **13**, 474 f. (1881).
[2] Ann. chim. phys., [6] **4**, 427 (1885).

solution, asserts Raoult; or they are acting as if they are being liberated, says Valson!

All these facts and views were established on the eve of the classical electrolytic dissociation theory of Arrhenius. In 1884, he brought forward the view that "every substance which reacts metathetically with an electrolyte, so that the ions of the latter are separated, is an electrolyte, as are also the products of the reaction."[1] From this it follows "that water, alcohols, phenols, aldehydes and many other substances are electrolytes and consequently conductors of the electric current." Salts have lost their dominant rôle.

This statement greatly extended the class of electrolytes. A field of compounds, originally small and well defined, including chiefly "salts," *i.e.* ordinary salts, acids, and bases of inorganic character, gathers within its environs new territories and, strictly speaking, loses its boundaries. In 1887 Arrhenius elaborated his theory of electrolytic dissociation.[2] Its approval was so general that the theory was soon accepted as explaining the mechanism not only of analytical, inorganic reactions, but also of metathetical organic changes.

Let us examine some recent views on this matter. Lowry's [3] postulate on the basis of the electronic theory contains the noteworthy statement "that in organic chemistry, as in inorganic chemistry, chemical reaction takes place between ions, either free or bound." More recently Meerwein[4] assumes that ions take part in organic reactions. He calls them "krypto-ionic-reactions." He holds that the ionizing ability of weak electrolytes is increased by formation of complex compounds and that catalytic action is linked directly with the formation of complexes and the strengthening of the electrolytic character of compounds. This view, however, is not accepted by Skrabal.[5] It seems

[1] *Recherches sur la conductibilité galvanique des électrolytes*, Pt. II, p. 11 (Stockholm, 1884.) *See also* Ostwald's *Klassiker* . . ., No. 160, p. 67.

[2] Z. physik. Chem., 1, 631 (1887).

[3] Instit. Intern. de Chimie Solvay, II Confér., 1925, p. 5; *see also* Trans. Faraday Soc., 19, pt. 2, 490 (1923).

[4] Ann., 455, 227 (1927).

[5] Z. Electrochem., 33, 322, 334 (1927).

to me that a simplification of our theories, and acceptance of the working hypothesis that ions participate in all chemical reactions, is logically necessary in consequence of our present electronic teachings. In this connection it might be well to refer to an old statement of Ostwald. In 1889 he expressed the opinion "that an electrolyte would eventually decompose electrolytically in various ways."[1] The following case may serve as an example. The compound sodium chloracetate, $NaOOC{\cdot}CH_2Cl$, breaks down mainly into the ions Na^+ and $\overline{O}CO{\cdot}CH_2Cl$, but also, to a very slight degree, into the ions $NaOCO{\cdot}CH_2^+$ and Cl^-.[2] Another statement of his is also remarkable: "It is highly probable that the action of catalysts, such as hydrogen chloride in the formation of esters, ferric chloride in chlorination, etc., consists of nothing more than the formation of compound electrolytes."[3]

The difference between various classes of compounds and reactions is not one of kind. Organic compounds as opposed to typical inorganic electrolytes, differ only in degree, as is shown by the speed of chemical reaction. "The supposition that all substances without exception are broken up into ions, even to a very small extent, follows as a necessary corollary to the principles of the dissociation theory; there exist no reasons why any differentiation should be made between electrolytes and non-electrolytes."[4] The same fundamental standpoint is also taken by Wm. Ostwald, but it is probably for didactic reasons that he lays emphasis on aqueous solutions of salts when he writes in one of his textbooks (1894):[5] "Electrolytes

[1] Z. physik. Chem., **3**, 598 (1889).

[2] We can develop this view by supposing that the ion $NaOCO{\cdot}CH_2^+$ dissociates into $Na^+ + \overline{O}COCH_2^+$ and that the latter "amphoteric" ion can be formulated as a so-called "inner anhydride" $\begin{matrix} O \\ \diagup\diagdown \\ CO \cdot CH_2 \end{matrix}$. Let us write the total equation of dissociation and add a surplus of free sodium hydroxide: $NaOCOCH_2Cl + NaOH \leftrightarrows Na^+ + \overline{O}COCH_2^+ + Cl^- + Na^+ + OH^-$. What can happen? The hydroxyl ion OH^- will form with the ion $\overline{O}COCH_2^+$ a new and less dissociable compound ion $\overline{O}COCH_2OH$, that is the ion of glycolic acid. Therefore the total equation represents the ionic reaction of glycolic-acid formation from sodium chloracetate plus sodium hydroxide. An analogous consideration suggests the formation of other substitution products of halogenated organic acids.

[3] Ibidem. *See also* Hantzsch, Ber., **58**, 637 (1925).

[4] Euler, Z. physik. Chem., **36**, 645 (1901); Lapworth, J. Chem. Soc., **79**, 1266 (1901).

[5] *Die wissenschaftlichen Grundlagen der analytischen Chemie.*

are salts in aqueous solution. The term 'salt' is here used to include both acids and bases, in that acids are salts of hydrogen, and bases salts of hydroxyl. Solutions of salts in alcohol are also dissociated, even if to a much smaller extent." "Salts are binary compounds, whose components are instantaneously exchangeable."[1] "Non-electrolytes include all organic compounds (with the exception of typical acids, bases, and salts) and further, solutions of all substances in such solvents as benzene,[2] carbon disulphide, and ether. Solutions in alcohol[2] furnish a transitional stage to electrolytes, in that dissociation of salts, even though very slight, does take place. Even the substances and solutions previously mentioned are not to be considered as absolutely undissociated, just as there are no absolute non-conductors. The limit can here be fixed only as in similar cases, as the point at which all available means of measurement and observation fail."

III. THE SOLVENT AS A CO-OPERATING FACTOR IN THE FORMATION OF ELECTROLYTES

Water as a Co-electrolyte

Fulham had already noted, at the end of the 18th century, as the result of experiments designed to lead to the metallization of textiles, that the reduction of metal. by hydrogen took place only in the presence of waters Gay-Lussac and Thénard[3] furthermore showed that, at their point of fusion, the chlorides of silver, sodium and barium were totally decomposed by fused borax with evolution of hydrogen chloride, provided water vapor was present. No decomposition took place in the absence of moisture. Water vapor was also found necessary in the decomposition of sodium chloride by sand or clay, and in the evolution of carbon dioxide from the carbonates of sodium, calcium, barium, etc.[4]

[1] Compare also the views of Hittorf (1859) p. 97.

[2] We can say that this former restriction is no longer existent, since there are known conducting salt-solutions in C_6H_6, CS_2, $(C_2H_5)_2O$, etc. Solutions of salts in alcohol are good conductors.

[3] Gilb. Ann., **35**, 8 (1810).

[4] The ignorance or disregard of this rôle of moisture has been the source of fundamental discoveries in chemistry. The old chemists, in the time of Geber, supposed they

Davy found that the absolutely dry gases nitric oxide, air, and sulphur dioxide, would not act upon one another. He also showed that dry chlorine would not bleach blue litmus paper.[1] Grotthuss[2] noted in 1819 that starch was not always colored blue by iodine: "Here the presence of water is absolutely necessary." Likewise Berzelius made the general statement in his textbook "that absolutely anhydrous substances seldom or never act upon one another at ordinary temperatures."[3] Water, apparently an inert substance, was thus early recognized as filling the rôle of catalyst or mediator in chemical reactions. However the recently created electrochemistry again learned to recognize the part played by water.

Faraday had already observed that certain compounds which acted as non-conductors in the homogeneous fluid condition, were not only conductors when dissolved in water but were also decomposed by the electric current. Thus concentrated sulphuric acid neither conducts nor is decomposed, whereas in aqueous solution it both conducts and is decomposed. The same observations were noted in the case of liquid sulphur dioxide as opposed to an aqueous solution of sulphurous acid. In these cases water fulfils a definite function; it acts in a very particular manner. The following substances were found to act differently:

	Anhydrous:	Aqueous solution:
Ammonia, NH_3	non-conductor, non-decomposable	very poor conductor
Acetic acid CH_3COOH	" " " "	conducts poorly
Hydrocyanic acid HCN	" " " "	" "
Sulphur dioxide SO_2	" " " "	conducts and is decomposed
Sulphuric acid H_2SO_4	" " " "	" "

The halogen hydrides, the so-called strong hydracids,

were working with dried or calcined salts and clay, but thanks to their imperfect methods the remaining moisture was acting as a catalyzer, and the discovery of mineral, inorganic, acids was the result. Would Lavoisier have discovered the phenomena of combustion in pure oxygen if he had used absolutely dry gases? Would St. Claire-Deville have discovered and developed his theory concerning thermal dissociation in the gaseous state (1857) if he had used absolutely dry ammonium salts or dry ammonia and dry hydrogen chloride?

[1] Trans. Roy. Soc. London, 101, 7 (1811).

[2] Ostwald's *Klassiker*, No. 152, p. 118.

[3] Berzelius, *Lehrbuch der Chemie*, I, pt. 1, p. 447 (1825).

HCl, HI, HBr, HF, were characterized by Faraday (1834) and Hittorf (1859) as good conductors and strong electrolytes in aqueous solution. However, Hittorf regarded it "as a remarkable fact" that hydrochloric acid in the gaseous condition insulated the current completely.[1] Ten years later Gore[2] found that pure, anhydrous, liquid hydrogen chloride and hydrogen fluoride were also non-conductors.[3] Kohlrausch[4] finally concludes, on the basis of conductivity measurements of acid solutions, that the conductivity decreases with increasing concentration and that "the conductivity curves approach or incline toward zero as the point of complete saturation is obtained." Accordingly, he postulates that liquid hydrogen chloride and nitric acid as well as pure liquid acetic and sulphuric acids are non-conductors; that "electrolytes become good conductors only upon mixing." He went so far as to say, "We know not a single liquid which would, by itself at ordinary temperatures, be a good conductor."

The interesting investigations of Bleekrode[5] finally furnished unquestionable evidence that the hydrides of chlorine, bromine and iodine do not conduct in the liquid condition. Liquid ammonia and the amines were also shown to be non-conductors, or very poor conductors. Both Kohlrausch and Hittorf[6] regarded liquid ammonia and liquid hydrogen cyanide as extremely poor conductors.

These facts all point to the question: What condition is peculiar to aqueous solutions of the halogen hydrides, all of which have been found to be non-conductors in the anhydrous state? What is the chemical composition of these substances in aqueous solutions which conduct the current so readily?

Kohlrausch[7] leaves it an open question "whether hydrogen chloride is present in solution as HCl, or $HCl \cdot H_2O$,

[1] Ann. Physik, **106**, 585 (1859).
[2] Phil. Trans., London, **159**, 173 (1869).
[3] The specific conductivity of liquid hydrogen fluoride, HF, was recently determined by Fredenhagen, Z. physik. Chem., **128**, 264 (1927).
[4] Ann. Physik, **159**, 233 (1876).
[5] Wied. Ann., **3**, 161 (1878).
[6] Wied. Ann., **4**, 412 (1878).
[7] Wied. Ann., **6**, 169, 190 (1879).

or $HCl \cdot 2H_2O$." He does not support the general theory that ammonia is present in water as NH_4OH, since its behavior as an electrolyte contradicts this idea. Its conductivity curve is very different from that of strong bases. It must, therefore, be present as NH_3 and act as a conductor.[1]

The whole question entered a new stage as the result of the publication by Arrhenius of his paper *Investigations upon the Galvanic Conductibility of Electrolytes*, (1884). Arrhenius[2] begins with a solution of gaseous ammonia. He allows ammonia to combine partially with water to form the hydrate NH_4OH, such that a changeable equilibrium is set up between NH_3, H_2O and NH_4OH:

$$NH_3 + H_2O \leftrightarrows NH_4OH$$

$$K = \frac{(NH_3)\cdot(H_2O)}{NH_4OH}$$

Accordingly the concentration of NH_4OH will increase with dilution. From this Arrhenius concludes: "The conductivity of an ammoniacal solution is caused by the presence therein of a small quantity of NH_4OH, which is increased by dilution of the solution."

This point of view is subsequently applied to aqueous solutions of acids, such as acetic acid and hydrochloric acid, both of which become electrolytes upon the addition of water. He says, "No one can deny the complete analogy of this phenomenon with that which occurs in the dilution of ammonia and of acetic acid, although this takes place much more promptly."

Arrhenius summarizes his ideas with reference to weak bases and acids as follows: "The aqueous solution of any hydrate contains, in addition to water, two parts, the one active (electrolytic), the other inactive (non-electrolytic). The three constituents, water, the active hydrate, and the

[1] Indeed, since we generally admit that ammonia may dissociate in accordance with the equation $NH_3 \leftrightarrows NH_2^- + H^+$, it seems logical to consider also the possibility of such dissociation in aqueous solution.

[2] *Op. cit.*, Seconde Partie, "Théorie chimique des électrolytes," p. 4f.

inactive hydrate, form a chemical equilibrium such that dilution increases the active part and diminishes the inactive part."[1]

This is the original form of the theory of electrolytic dissociation and at the same time a chemical theory for the formation of electrolytes by solvation (hydrate theory). It is a peculiar fact that, in the further development of the dissociation and ionic theories, the original fundamental idea of the hydration of electrolytes was not only for a time abandoned, but was vigorously opposed when evidence in favor of such a hypothesis was submitted from the chemical side. However, it must be admitted that the indefinite character of this theory of the formation of "hydrates" in solution, did not appear to support a quantitative connection of this idea with the requirements of the ionic theory. It is also evident that it was much easier and more convenient to present and prove the dissociation theory in the light of free and non-solvated ions. That this path of reasoning would have to lead back again to the old problem of the rôle of water in the formation of electrolytes, and particularly in the case of the halogen hydrides which, though insulators, nevertheless become good conductors in solution, was to be expected as the result of the original trend in the research, since it became evident that the conception of the freedom of the ions and the passivity of the solvent was unsatisfactory.

One of the earliest and most suggestive thinkers along the line of the action of water in the formation of electrolytes, is Henry E. Armstrong. As early as 1886 he advanced this theory and attempted to find evidence to support it.[2] He held that there are two types of electrolytes: first, certain simple liquid salts; and secondly, compound ones, such as solutions of salts in water. "Chemical action always takes place and only takes place in a conducting or electrolytic circuit," *i.e.* "chemical action is reversed

[1] See also Ostwald's *Klassiker*, No. 160, p. 61.

[2] Electrolytic conduction in relation to molecular composition, valency and the nature of chemical change, Proc. Roy. Soc. London, 40, 268 (1886).

electrolysis." In a compound electrolyte, such as water and hydrochloric acid, both components act reciprocally upon each other as follows

$$H_2O + HCl \leftrightarrows HCl{\cdot}OH_2$$

If one assumes that liquid water is a mixture of various complex molecules and that these form the equilibrium $(H_2O)_x \leftrightarrows x(OH_2)$, in which the complex molecules are called "polyhydrones," and the simple water molecules "hydrones," one may picture hydrochloric acid as follows[1]

$$HCl + OH_2 \leftrightarrows HCl\begin{matrix}H\\ \diagup\\ \diagdown\\ OH\end{matrix} \quad \text{and} \quad H_2O + HCl \leftrightarrows H_2O\begin{matrix}Cl\\ \diagdown\\ \diagup\\ H\end{matrix}$$

He says further that "the occurrence of electrolysis involves the interaction of the two kinds of complexes while under the influence of an electromotive force." Consequently "no acid, so-called, functions as an acid *per se*. The compounds named acids are all inert—for the simple reason that they cannot conduct electricity. . . . No binary hydrogen compound in the liquid state is an electrolyte *per se*."[2]

In this connection it may be mentioned that Walden, in conjunction with Centnerszwer, in 1901 came to the conclusion, as the result of ebullioscopic and conductometric investigations carried out on a variety of substances dissolved in liquid sulphur dioxide, that dissolved substances as electrolytes formed polymeric molecules as well as association-products with the solvent. The latter was particularly noticeable because of color changes in the solution.[3] With reference to the electrolytic nature of the hydrides HX, H_2Y, and H_3Z, to which both acids and bases belong, we find that Walden (1923) pointed out that in contrast to salts these "may be designated as krypto- or

[1] The one might be termed the chloronium form, the other the oxonium form.

[2] H. E. Armstrong, *The Art and Principles of Chemistry*, p. 243, 262, (London, 1927). (Comp. also Kohlrausch's view, p. 151 ff.)

[3] Bull. acad. sci. St. Petersburg, June 1901; reprinted in Z. anorg. Chem., 30, 145-250 (1902).

pseudo-electrolytes which become electrolytes only as the result of physical or chemical metathesis with the proper solvent."[1]

Oxonium Theory of Acids and Bases (Werner)

"Water plays the part of a base towards acids, and the part of an acid towards bases. The advantage of water lies in the fact that it is fluid at lower temperatures and also more easily replaceable than most other [oxides.]"[2] This statement by the old master, Berzelius, may serve as the motto for the modern chemical oxonium theories. This old view has also found expression in the electrochemical theory of the dissociation of water: $H_2O \leftrightarrows HO^- + H^+$ and thus both ions of water became prototypes for basic and acidic character in general.

Bases. Alfred Werner advanced a "theory for acids and bases" radically different from all the commonly accepted theories of dissociation. He held that equations of the type

$$\text{metallic hydroxide, } MOH = M^+ + OH^-,$$

$$\text{or} \qquad KOH = K^+ + OH^-$$

are incorrect.[3] He believes that the latter should be expressed as

$$KOH + H_2O = \left[\begin{matrix} K \\ H \end{matrix}\!\!>\!O\cdot H\right]OH = \left[\begin{matrix} K \\ H \end{matrix}\!\!>\!O\cdot H\right]^+ + OH^-$$

"The metallic hydroxides, among which may be included those of ferric iron, magnesium, calcium, potassium, etc., do not dissociate as such, but are compounds which by addition of water form the dissociating bases (aquo-bases). Metallic hydroxides are therefore related to true bases in

[1] P. Walden, *Elektrochemie nichtwässeriger Lösungen*, p. 219 (1924).

[2] Berzelius, *Lehrbuch*, I, p. 458. Compare also Hittorf's views on water.

[3] If this statement is true, one might indeed ask how Humphrey Davy ever succeeded in preparing free potassium and sodium by the electrolysis of the respective molten hydroxides.

the same manner as ammonia is to ammonium hydroxide, phosphine to phosphonium hydroxide, etc."[1] If compounds of the type of ammonia are termed "anhydro-bases," then one must distinguish, according to Werner, between anhydro-bases and aquo-bases. "Anhydro-bases are compounds which combine with the hydrogen ions of water (that is with the acid component) in aqueous solution and thereby cause a shift in the dissociation equilibrium of water until their corresponding characteristic hydroxyl ion concentration has been reached." "Aquo-bases (commonly termed merely "bases") are addition compounds of water, which in turn dissociate in aqueous solution to give hydroxyl ions." These definitions may be symbolized by the equations[2]

$$B\ (=\text{anhydro-base}) + H_2O \rightleftarrows B + (H^+ + OH^-) \rightleftarrows$$

$$B{\cdot}H^+ + OH^-,$$

$$(\text{Aquo-base} + H_2O) = (\text{aquo-base}{\cdot}H)^+ + OH^-$$

Acids. "Acids are hydrogen compounds whose hydrogen is capable of combining anhydro-bases with the resultant formation of salt-like compounds. The modern theorists speak of the addition of "protons". Addition reactions of this kind include those with ammonia, amines, metallic hydroxides, alcohols, etc."[3] As in the case of bases, Werner distinguishes between anhydro- and aquo-acids. Anhydro-acids are therefore "compounds which, in aqueous solution so combine with hydroxyl ions of water as to cause a shift in the dissociation equilibrium of the solvent water until the corresponding, characteristic (for the given acid) hydrogen ion concentration has been

[1] Werner, *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*, p. 369 (3d ed., 1913); p. 275 (4th ed., 1920). *See also* Werner, Z. anorg. Chem., 3, 267 (1893); 15, 1 (1897).

[2] Attention must be directed to the view of Werner that water molecules are of the simplest form, H_2O, and not auto-complexes $(H_2O)_n$. The reactions of dissociation and addition of water are founded on this conception of the simplicity of water molecules.

[3] Werner, *Neuere Anschauungen etc.*, 4th edit., p. 279. Alcohols are here considered as anhydro-bases.

attained."[1] The following are included among the anhydro-acids:

(1) Hydrogen acids, HX, (hydrochloric acid, etc., and hydrogen sulphide, hydronitric acid).

(a) $HX + OH_2 = HX{\cdot}OH_2$ and $HX{\cdot}OH_2 \leftrightarrows XH{\cdot}OH^- + H^+$, or

(b) $HX + (HO^- + H^+) = HX \cdot OH^- + H^+$.

(2) Acidic oxides:[2]

(c) $O_3S + (OH^- + H^+) = O_3S{\cdot}OH^- + H^+$

$O_2S + (OH^- + H^+) \leftrightarrows O_2S{\cdot}OH^- + H^+$, or

$O_2C + (OH^- + H^+) \leftrightarrows O_2C{\cdot}OH^- + H^+$.

Perhaps also

(d) $HNO_3 + (OH^- + H^+) \leftrightarrows (NO_3H \cdot OH^-) + H^+$

(3) In the group of anhydro-acids[3] may also be included those metallic compounds capable of forming salts, such as $Zn(OH)_2$, $Al(OH)_3$, $Pt(OH)_4$, $Pb(OH)_4$, $PtCl_4$, $PtCl_2$, $Hg(CN)_2$, etc. This conception, however, has recently been attacked by Hantzsch.[4]

Salt-formation. In accordance with this theory of acids and bases there should be formed hydrated cations and hydrated anions of anhydro-bases and anhydro-acids, respectively, which in turn should then yield hydrated or aquo-salts.

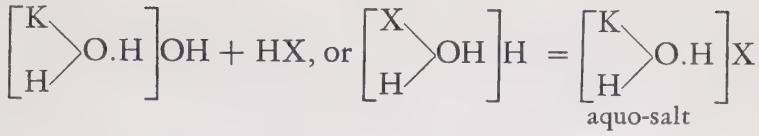
[1] Ibid., p. 280.

[2] It is worthy of emphasis that the old problem (oxygen or hydrogen theory of acids, *i.e.* Lavoisier—Berzelius or Davy—Liebig) arises in a new form in Werner's views. The acid oxides (that is, the acids of Lavoisier) and hydro-acids, HX, come to be considered as chemically of the same kind; both classes are anhydro-acids, and all become acids by combination "with the hydroxyl ions of water." The hydroxyl ion is the connecting link between the two theories, and its addition is regarded as the essential chemical cause of the formation of acids. It is not a chemical individual that is an acid—it is the solvent (water and its hydroxyl ions) which calls into existence the acid potencies by a chemical reaction, *i.e.* by an act of addition.

[3] There exist also metallic hydroxides, such as $Zn(OH)_2$ and $Al(OH)_3$, which can add on both hydrogen and hydroxyl ions and form salts. These are known as amphoteric hydroxides and will be discussed later as amphoteric electrolytes.

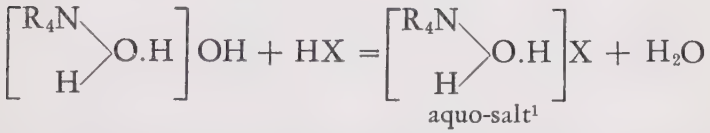
[4] Ber., 58, 620 (1925); 59, 1116 (1926).

Thus,



or

Again,



Salts may be derived from amphoteric metallic hydroxides by the addition of either acids or alkali hydroxides. For instance,

$$Zn(OH)_2 + 2HX = [Zn(OH_2)_2]X_2,$$

or

$$Al(OH)_3 + 3HX = [Al(OH_2)_3]X_3, \textit{i.e.}\ \text{aquo-salt.}$$

With sodium hydroxide

$$Zn(OH)_2 + NaOH = [Zn(OH)_3]Na$$
$$Al(OH)_3 + NaOH = [Al(OH)_4]Na$$

i.e. hydroxo-salts.

All of these postulates of Werner are based upon water as the solvent and additive companion of acids and bases. It is indeed a conspicuous point that both hydrogen and hydroxyl ions are treated by him as anhydrous. Let me, however, mention in this connection that at the present time it is the hydrogen ion which is assumed to exist in the hydrated or hydroxonium ion form, OH_3^+, (or as $H^+.8H_2O$).[2] Two other points may be mentioned in connection with Werner's theory of anhydro-acids and bases.

[1] May we not assume that in alcoholic or analogous non-aqueous solutions, "alco"-salts corresponding to "aquo"-salts will be formed by the same reactions?

[2] Hantzsch, Z. Elektrochem., **29**, 230 (1923).

The supposed addition of the hydroxyl ions (of water) to anhydro-acids, and of hydrogen ions to anhydro-bases, and the resulting steps in the dissociation equilibrium of water as a measure of the strength of dissolved acids or bases, presupposes extraordinary ease of such an electrolytic dissociation of water molecules. In other words: the act of solution of anhydro-acids and anhydro-bases may be construed as a direct electrolysis or electrolytic dissociation of water. Furthermore the views of Werner would support a statement which has been in dispute for a long time, namely, that it is water which is directly decomposed upon electrolysis of acid solutions.

If we attempted to apply the definition of anhydro-bases and anhydro-acids directly to non-aqueous media as solvents, such as alcohol, one would have to assume different kinds of electrolytic dissociation of the alcohol molecules. Let us consider an anhydro-acid, such as HCl, in alcohol; such a solution is a good electrolyte and reacts to form a salt (KCl) with an alcoholic solution of the anhydro-base KOH. In the acid solution we must suppose the existence of hydroxyl ions of the solvent, *i.e.*

$$C_2H_5OH \leftrightarrows C_2H_5^+ + OH^-;$$

further, $$HCl + OH^- \rightarrow (HCl \cdot OH^-).$$

In this case, however, a hydrogen ion, H^+, cannot be present. Therefore another form of dissociation must be supposed for alcohol: $C_2H_5OH \leftrightarrows C_2H_5\ O^- + H^+$ and $(HCl \cdot C_2H_5O^-) + H^+$. The solution of the anhydro-base KOH must contain the characteristic OH^- ion; this ion is present in water ($HOH \leftrightarrows H^+ + OH^-$) since the hydrogen ion is combined with the anhydro-base. If this rule is taken as generally applicable to all dissociating solvents, difficulties arise in the consideration of alcoholic solutions. Supposing that the hydroxyl ion must come from the solvent ($C_2H_5OH \leftrightarrows C_2H_5^+ + OH^-$), the remaining cation, $C_2H_5^+$, must be combined with the anhydro-base: $KOH + C_2H_5^+ \rightarrow (KOH \,.\, C_2H_5^+)$. The possibility of such a complex cation is formally admissible, but from a chemical standpoint scarcely plausible. Let us—according to

Werner's rule—allow the hydrogen ion, H^+, of the solvent ($C_2H_5OH \leftrightarrows C_2H_5O^- + H^+$) to combine with the anhydrobase, i.e. $KOH + H^+ \rightarrow (KOH.H^+)$; then the alkaline solution will not possess the characteristic hydroxyl ion, OH^-, but the anion $C_2H_5O^-$. The classical dissociation theory of Arrhenius recognized no such difficulties; it postulated as most reasonable and most simple the direct dissociation of the base KOH:

$$KOH \leftrightarrows K^+ + OH^-$$

One may ask: What has been the scientific effect of Werner's theory on "salts, acids and bases"? Disregarding any question as to the importance of these views in the synthesis of new kinds of salts, etc., we must concede that Werner by his work has undoubtedly influenced the development of the evolution of the classical electrolytic dissociation theory. "Ideal solutions," as defined in van't Hoff's osmotic theory, neglected the chemical action between solvent and solute. According to this theory, the act of solution, like vaporization, is a typical physical phenomenon. The theory of electrolytic dissociation examined the electrolytes with regard to their degree of dissociation into free ions. From the chemical formula the constitution of the ions could be ascertained and the solvent, water, merely served as a neutral medium for the formation and motion of these ions. In direct contradiction to this theory Werner maintains that water as solvent is the principal agent in electrolytic dissociation; it is the primary electrolyte, and only by the chemical addition of water molecules or water ions to the molecules of the solute does the latter become an electrolyte. It is a well-known fact that the classical electrolytic dissociation theory has produced its greatest scientific results without aid from, or reference to Werner's theory. However, new classes of chemical substances, new kinds of solvents and new physical phenomena, have brought new electrochemical problems. The attempts to find a plausible interpretation for such facts has compelled us to modify our views as to the rôle of the solvent. Water, and later the

non-aqueous solvents, have become more and more the active factors. We may assume either chemical combination with the solute (Hantzsch's oxonium theory, etc.), or addition of the ions of the solvent to dissolved bodies, or the di-pole character of solvent molecules (Debye).

IV. TRUE AND PSEUDO-ELECTROLYTES. OXONIUM AND TRANSITION-THEORY OF HANTZSCH

True acids and Salts; Pseudo-acids and Pseudo-salts.

The term pseudo-acids, -bases, and -salts was evolved as a result of the investigations of Hantzsch and of Ley in 1899, and was given its experimental basis chiefly by conductivity measurements of aqueous solutions. "If a neutral hydrogen compound is liberated by the action of hydrochloric acid upon a non-hydrolyzed alkali salt, such a substance, resulting by rearrangement, may be termed a pseudo-acid."[1] The outstanding point in this statement is the idea of a rearrangement taking place under these conditions. As characteristic of a pseudo-salt, such as mercuric nitroform, $Hg[C(NO_2)_3]_2$, Ley[2] observed first a change in color. This compound is colorless in the solid form and yields a colorless solution when dissolved in non-ionizing solvents. However, its solution in water or in pyridine is colored. Another point of difference lies in the degree of dissociations of the acids (such as the very strong acids HCl and HSCN) on the one hand, and their respective salts, (for instance $HgCl_2$ and $Fe(SCN)_3$, both of which are but very slightly dissociated)[3] on the other.

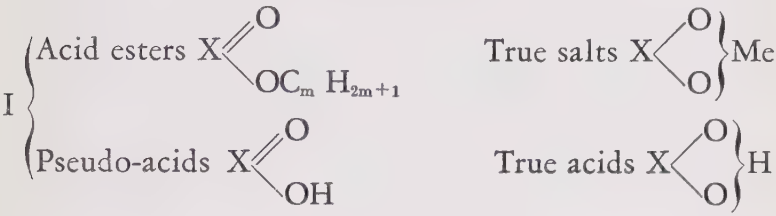
If the action of the sodium hydrate upon a true salt results in the formation of a non-alkaline inert hydrate,[4] this substance, formed by rearrangement, may be called a "pseudo-base."[5] This rearrangement is a time reaction, whose course may be followed by the gradual decrease in conductivity.

[1] Hantzsch, Ber., **32**, 575 (1899).
[2] Ber., **32**, 1357 (1899).
[3] Ley, Z. anorg. Chem., **164**, 380 (1927).
[4] From the standpoint of Werner's theory one could, perhaps, say that pseudo-acids and -bases are anhydro-acids and anhydro-bases whose ability to combine with hydroxyl or hydrogen ions of water is extremely small.
[5] Hantzsch and Kalb, Ber., **32**, 3109 (1899).

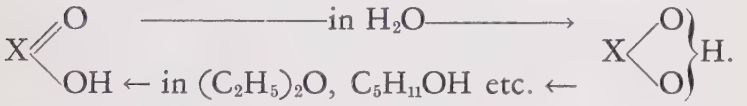
Hantzsch was subsequently able to expand and bring his theory of acids, esters and salts to the state in which it is outlined below. He accomplished this by the introduction of optical methods, by the use of chemical reactions, and by the employment of a variety of solvents.

Non-electrolytes — Complete electrolytes

Optically very different[1]



Partial electrolytes



Acids in equilibrium

The halogen hydrides, HCl, HBr, and HI are, like nitric acid, pseudo-acids.[2]

Homeopolar non-electrolytes			Heteropolar electrolytes	
Ester	Pseudo-acid	$+mH_2O$	so-called true acids	alkali salts MeX
		$\rightleftarrows$		
C_mH_{2m+1} X	H−X	$-mH_2O$	HX, H_2O= $(OH_3)X$	in H_2O
Optically almost identical			Optically identical	

"Acids are hydrogen compounds which have a tendency to form salts either by addition or substitution."[3] The "acidity of an acid is determined by its tendency to form

[1] Z. Electrochem., **29**, 222 (1923).
[2] Ber., **58**, 620 (1925).
[3] Z. Elektrochem., **30**, 214 (1924).

true salts."[1] Hydrogen ions, accordingly, assume only a secondary or conditional rôle.[2]

Class I. "*True electrolytes*, that is, substances which in themselves are already electrolytes in the homogeneous condition . . . namely, true acids, true bases, and true salts . . . are naturally taken into solution by all solvents as electrolytes." "Addition products are first produced which subsequently break up into ions as the concentration and dissociating power of the solvent increases."[3]

"True acids are heteropolar hydrogen compounds containing a labile, active hydrogen atom that can be directly replaced by strongly positive metals or complex cations, resulting without constitutional change in the formation of salts. Hydroxonium salts are also formed in water or in aqueous solution."[4] True acids include sulphuric acid $(SO_4)H_2$, the sulphonic acids $(RSO_3)H$, perchloric acid $(ClO_4)H$, trichloracetic acid $(CCl_3COO)H$,[5] as well as the complex acids[6] $(AuCl_4)H$ and $(PtCl_6)H_2$.

True salts include the perchlorates of the alkali metals $(ClO_4)Me$,[7] oxonium salts such as $ClO_4[HO(C_2H_5)_2]$,[8] oxonium halides, nitronium perchlorate, alkali halides X(Me),[9] and alkaline earth halides,[10] alkali nitrates $(NO_3)Me$,[11] and alkali sulphates $(SO_4)Me_2$.[12] In order to determine chemically whether or not the metallic halides exist in the form of true or pseudo-salts, Hantzsch and Carlsohn[13] employed concentrated sulphuric acid as reagent. In aqueous, alcoholic or ethereal solution true salts are

[1] *Ibid.*, p. 211; compare the views of Berzelius and Werner.
[2] *Ibid.*, **29**, 239 (1923).
[3] Z. Elektrochem., **30**, 202 (1924).
[4] Z. Elektrochem., **29**, 246 (1923). Conversely one might ask, is the replacement of an active hydrogen atom in esters (*i.e.* malonic, aceto-acetic, etc.) or alcohols by sodium, a sufficient proof of acid character?
[5] *Ibid.*, p. 227.
[6] *Ibid.*, p. 231.
[7] Hantzsch, Z. Elektrochem., **30**, 210 (1924).
[8] *Ibid.*, **29**, 236 (1923). Silver perchlorate is, however, a pseudo-salt, Ber., **59**, 1096 (1926).
[9] Ber., **59**, 1096, 1103 (1926).
[10] Z. anorg. Chem., **160**, 15 (1927).
[11] *Ibid.*, 1105.
[12] *Ibid.*, 1096. The heavy metal sulphates are homeopolar pseudo-salts.
[13] *Ibid.*, 10.

acted upon by sulphuric acid with resulting evolution of the free acid. The pseudo-salts are merely dehydrated under the same condition and are precipitated in an undecomposed state.

Class II. "*Pseudo-electrolytes* are substances which in the homogeneous condition, or in wholly indifferent solvents such as the saturated hydrocarbons, are non-electrolytes, but when dissolved in various solvents, particularly those containing oxygen, sulphur and nitrogen, are converted more or less completely into electrolytes." "These pseudo-electrolytes are either pseudo-acids, pseudo-bases, or pseudo-salts." "Here, as in the other cases, an addition product or solvate is first formed which by rearrangement yields an electrolyte—from which in turn the solvated ions are obtained."[1]

Pseudo-acid	*Pseudo-salt*[2]
↓	↓
Solvate of a pseudo-acid	Solvate of a pseudo-salt
↓	↓
Solvate of a true acid	Solvate of a true salt
↓	↓
Ions of a true acid	Ions of a true salt

In the homogeneous condition pseudo-acids are associated, usually in the dimolecular form. The carboxylic acids are typical pseudo-acids. Even the strongest mono-carboxylic acids exist in two forms which are in equilibrium with one another. The strongest of the dicarboxylic acids are inactivated to pseudo-acids even in fairly concentrated ethereal solutions.[3] The halogen hydrides and nitric acid O_2NOH are also pseudo-acids.[4]

Many years ago I called attention[5] to the high specific conductivity of pure sulphuric acid, $\kappa_{25} = 1006 \times 10^{-5}$

[1] Z. Elektrochem., **29**, 244 (1923); **30**, 202 (1924). Ber., **58**, 953 (1925).

[2] Pseudo-salts include the halides (1) of metals capable of existing in two or more valencies, such as $SnCl_2$ and $SnCl_4$, as well as those (2) of cobalt, aluminum, and other tri- and tetravalent elements (Hantzsch and Carlsohn, Z. anorg. Chem., 160, 15 (1927)).

[3] Zeit. Elektrochem., **29**, 228 (1923).

[4] *Ibid.*, p. 232; see also Ber., **58**, 620 (1925).

[5] Walden, Z. anorg. Chem., **29**, 383 (1902).

(or 1.006×10^{-2}). Later I emphasized the high conductivity of pure nitric acid,[1] $\kappa_0 = 1.36 \times 10^{-2}$, a value afterwards confirmed by Hantzsch,[2] who found $\kappa_0 = 1.05 \times 10^{-2}$. Recently Fredenhagen[3] determined the specific conductivity of pure liquid hydrogen fluoride and found $\kappa_0 = 0.15 \times 10^{-2}$, a value somewhat smaller than that given by Hill and Sirkar (1910) $\kappa_0 = 2.69 \times 10^{-2}$. From these three pure, liquid substances H_2SO_4, HNO_3, and HF, whose specific conductivity κ in the homogeneous condition is of the order 10^{-2} (at ordinary temperature), we can conclude that the above statements in their categorical form are a contradiction of the facts.

One may then ask whether all these arguments are entirely convincing, or do they admit also of another explanation for the observed phenomena?

This theory of two isomeric forms of acids, viz., pseudo-acid $\leftrightarrows$ true acid, is not accepted by Fajans[4] who justly contends that the optical differences, which have been used as the basis for the existence of such an isomerism, may very well be explained and even necessitated by the process of dissociation. The observations of H. Ley and Hünecke[5] are also of importance in passing judgment on this question. These investigators made optical absorption measurements in the ultra-violet on certain carboxylic acids, their esters and their salts, and state that "there is absolutely no reason why we should assume that the solvent effects noted in the case of these acids should be explained by rearrangement (acid $\leftrightarrows$ pseudo-acid)." Even esters which are incapable of rearrangement show no optical constancy and are influenced by solvents to as great an extent as the acids themselves. "The change in the spectrum of the carboxylic acids wrought by salt formation is of a magnitude equal to that called forth by the solvents." Ley, Von Halban[6] and Fajans,[7] explain these changes in

[1] Walden, Z. angew. Chem., **37**, 390 (1924).
[2] Hantzsch, Ber., **58**, 955 (1925).
[3] Fredenhagen, Z. physik. Chem., **128**, 11 and 264 (1927).
[4] Naturwissenschaften, **11**, 179 (1923).
[5] Ber., **59**, 510 (1926).
[6] Z. Electrochem., **29**, 443 (1923).
[7] Naturwissenschaften, **11**, 165 (1923).

dissociating acids by the deformation of the outer shell of electrons of the acid anion produced by the approach of the hydrogen nucleus. Interesting, also, is the statement by Ley[1] that ability of the ester group, COOR, to solvate might well be expected to be different from that of the carboxyl group, COOH. He also suggests that it is not the whole dissolved molecule which is entirely surrounded by solvent molecules, but that the latter are attached only to certain "lyophile" groups.

Brönsted and Pedersen[2] accept in general the theory of pseudo- and true acids and give the following definition for pseudo-acids: On the basis of the equilibrium

$$\begin{array}{c}(A'H) \leftrightarrows A' + H^+ \\ \updownarrow \\ (A''H)\end{array}$$

A″H may be regarded as the non-acid and A′H as the acid form of the pseudo-acid; since the equilibrium $A''H \leftrightarrows A' + H^+$ also exists, such pseudo-acids may also display the characteristic properties of ordinary acids.[3] The "non-acid" nature of the compound A″H may "best be defined by delegating to it the property of either breaking up into ions by direct reaction, or of being formed from ions by addition reactions." In a like manner "a pseudo-base would be a substance, incapable of directly adding on hydrogen ions," but one which could exist in equilibrium with a true base. Thus, the true base, ammonia, and the pseudo-base, ammonium hydroxide, are in equilibrium with one another:

$$\begin{array}{c}NH_3 + H^+ \leftrightarrows NH_4^+ \\ \updownarrow \\ NH_4OH\end{array}$$

If we take nitromethane $C(NO_2)H_3$ as an example of a pseudo-acid, we will find the immediate ionization in

[1] *Ibid.*, p. 517 (1926).
[2] Z. physik. Chem., **108**, 217 (1924).
[3] See also Kauffmann, Z. physik. Chem., **47**, 618 (1904).

water extremely slight; thus, where $v = 10.3$, $\lambda_v^{25} = 0.0031$. For the calcium salt, $C(NO_2)H_2 \cdot Ca/2$, where $v = 16$ lit., $\lambda_{16}^{25} = 45.7$. It evidently ionizes in accordance with the equation $C(NO_2)H_2 \cdot Ca/2 = C(NO_2)H_2^- + 1/2Ca^+$. The addition of hydrochloric acid reverses the reaction—

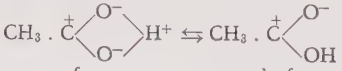
$$[C(NO_2)H_2 \cdot Ca/2 + HCl] \rightleftarrows C^-(NO_2)H_2 + 1/2Ca^+ + H^+ + Cl^- \rightarrow C(NO_2)H_2.H + Cl^- + 1/2Ca^+$$

The undissociated "pseudo-acid" $C(NO_2)H_3$ is formed by addition from the ions $C^-(NO_2)H_2$ and H^+. The definition quoted above does not seem to fit for cases of this kind.

Another statement may be cited which rejects the idea of a "pseudo-acid form."[1] Hamer and Bury write "It appears to be a corollary of the complete ionization theory of Milner, and of Debye and Hückel, that the terms 'pseudo-acid' and 'weak acid' are synonymous."[2]

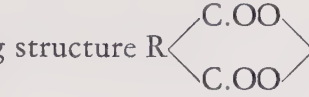
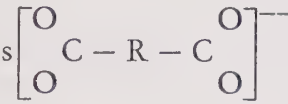
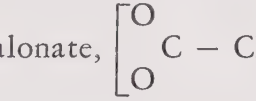
Let us examine next the alkaline-earth and heavy-metal salts of the inorganic and the organic di- and polybasic acids. Hantzsch states that the heavy-metal sulphates are homeopolar pseudo-salts. On the other hand he found in his former investigation that solid copper sulphate has the same optical absorption as a dilute solution of copper sulphate which contains Cu^{++} ions. The chromates of magnesium and of the alkali metals have the same absorption spectra. Their solutions evidently contain the same colored anion CrO_4.[3] However, the magnesium chromates show an abnormal conductivity (Walden). As far back as 1887 Walden[4] observed that the magnesium salts of the dicarboxylic acids of the oxalic acid series, as well as those of the tricarboxylic acids, citric and aconitic acids, possessed abnormal conductivity values. Bredig[5] attempted to

[1] Assuming that the views of Hantzsch adequately describe the relationships between acids, salts and esters, Lowry (Trans. Faraday Soc., 19, Pt. 2, p. 493 (1923)) gives the following equilibrium formulas between true and pseudo-acetic acid in aqueous solution on the basis of "intra-molecular ionization":



true form pseudo-form.

[2] J. Chem. Soc., 337 (1927).
[3] Hantzsch, Z. physik. Chem., **63**, 367; **72**, 362; **84**, 321.
[4] Z. physik. Chem., **1**, 536 (1887).
[5] Z. physik. Chem., **13**, 191, 202 (1894).

explain these anomalies by assuming the formation of complex ions.[1] On the basis of Hantzsch's theories these would probably be regarded as pseudo-salts. Instead of giving the divalent metallic salts of the dicarboxylic acid the (usual) ring structure  , Pfeiffer[2] formulates them as  in which the metallic atom is not directly bound with individual oxygen atoms, but exists in a state of affinity with all oxygen atoms of the acid radical. Supporting this hypothesis are the results obtained by Bragg from a study of the crystal structure of calcium carbonate. Each calcium ion was found to be surrounded by six carbonate ions, CO_3^{--}, and each carbonate ion in turn by six of those of calcium. A compound like magnesium malonate,  , might be expected to dissociate normally and give normal conductivity and transference values. This is not so. The formation of complex ions is always assumed when transference values are abnormal.

In the case of magnesium oxalate, studied by Kohlrausch, the equivalent conductivity shows an abnormal rate of decrease with increasing concentration. It is assumed by Kohlrausch that the formation of complex molecules is enhanced to such an extent that with rise in concentration of solution, the latter approaches the character of a colloidal solution.[3] New facts with reference to the question of the autocomplex formation of salts of the oxalates of divalent metals are presented in the investigations of Scholder.[4]

[1] See also Blomberg, Z. Elektrochem., **21**, 437 (1915).
[2] Ber., **55**, 1768 (1922).
[3] Ber. d. Berl. Akad., 1223 (1904).
[4] Ber., **60**, 1489, 1499, 1510, 1525 (1927).

So-called "inner salts" or "amphoteric electrolytes." (Betaines, Ampholytes)

The term 'inner salt' was previously applied to compounds whose molecules structurally contained both an acid group, such as the $-COOH$ or the $-SO_3H$, and, separated from the latter, a basic amino group. By mutual saturation or inner neutralization, cyclic salt-like structures containing pentavalent nitrogen, as in the ammonium salts, were supposed to have resulted. One of the commonest of these, glycocoll, amino acetic acid, $CH_2(NH_2)\cdot COOH$, was formulated as follows:

$$H_2N \cdot CH_2COOH \rightarrow CH_2\begin{cases} CO \\ NH_3 \end{cases} O$$

The fact that aqueous solutions of such "inner salts" were poor conductors had long been known in the case of glycocoll and asparagine. Bredig[1] was the first to advance the idea that the betaine was an "inner salt," that it carried, on the same molecule, both positive and negative charges which might neutralize each other. He later expressed his opinions in greater detail,[2] describing "amphoteric electrolytes as substances which simultaneously may be both acid or basic in aqueous solution, that is, substances which can (1) split off, or (2) combine with both hydrogen and hydroxyl ions. To be acids, they dissociate as $ROH \rightarrow RO^- + H^+$, and when acting as bases: $ROH \rightleftarrows R^+ + OH^-$."[3]

Bredig continues: "A further reaction may take place in the case of those substances, like the amino acids, whose molecule may possess at the same time both an acid and a

[1] Z. physik. Chem., **13**, 323 (1894).

[2] Z. Elektrochem., **6**, 33 (1899).

[3] Among inorganic compounds Bredig includes as amphoteric electrolytes the hydroxides of zinc, aluminum, and lead, as well as stannic and arsenic acids. The dissociation of lead hydroxide is formulated in the following manner—

as a base, $Pb(OH)_2 \rightleftarrows Pb^{++} + 2OH^-$

as an acid, $Pb(OH)_2 \rightleftarrows PbO_2^{--} + 2H^+$ or $Pb(OH)O^- + H^+$.

Pfeiffer (Ber., **40**, 4042 (1907)) is of the opinion that it is not the splitting off of hydrogen or hydroxyl ions, but rather the addition of either, which characterizes amphoteric substances. Thus,

$Zn(OH)_2 + 2H^+ = [Zn(OH_2)]_2^{++}$ in forming (aquo-) salts with acids and $Zn(OH)_2 + {}^-OH = [Zn(OH)_3]^-$ in forming salts with alkalies. See Werner's oxonium theory.

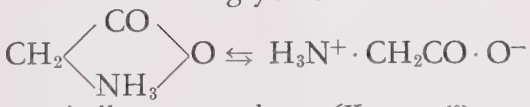
basic radical, that is, may contain an hydroxyl ion in addition to a dissociable hydrogen ion. This phenomenon, which to my knowledge was first pointed out by me, consists of the formation of an entity which is both positively and negatively charged, termed by Küster[1] a 'Zwitterion,' and identical with the so-called inner salts and anhydrides. Glycocoll dissociates in accordance with the equation:

$$HO{\cdot}H_3N{\cdot}CH_2\,COO{\cdot}H \leftrightarrows {}^{+}H_3N{\cdot}CH_2{\cdot}COO^{-} + H^{+} + OH^{-}.$$

A detailed experimental investigation on this subject was subsequently carried out by K. Winkelblech,[2] a co-worker of Bredig.

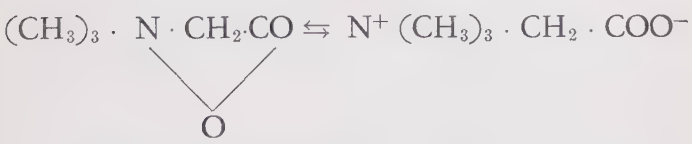
From considerations involving modern conceptions of the structure of crystals, the structure of individual molecules in the crystal lattice, and the effect of electrostatic forces within the molecule, Pfeiffer[3] arrives at his dipolar theory of betaines, which may be represented in the case of the amino acids by the formula $^{+}H_3N-R-COO^{-}$. He says: "Amino acids and betaines form molecular lattices which are in general similar to ionic lattices."[4] Several examples will serve to illustrate the type and varied electrolytic nature of such "inner salts." (K = dissociation constant)

glycine



practically a non-conductor ($K \sim 10^{-10}$)

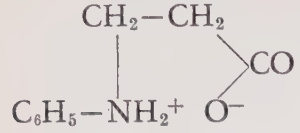
betaine



practically a non-conductor ($K \sim 10^{-10}$)

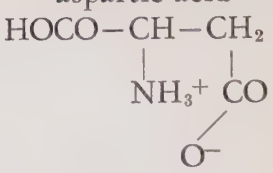
[1] Z. anorg. Chem., **13**, 136 (1897).
[2] Z. physik. Chem., **36**, 546 (1901).
[3] Ber., **55**, 1762 (1922).
[4] Concerning such ampholytes see also Bjerrum, Z. physik. Chem., **104**, 147 (1923); H Ley, Ber., **57**, 1705 (1924); Adams, J. Am. Chem. Soc., **38**, 1503 (1916).

β-anilidopropionic acid



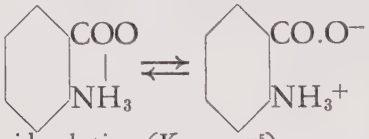
conductor ($K = 10^{-6}$)

aspartic acid



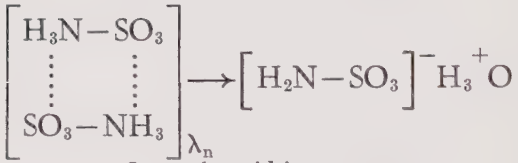
acid solution ($K \sim 10^{-4}$)

o-amino benzoic acid



acid solution ($K \sim 10^{-5}$)

aminosulfonic acid

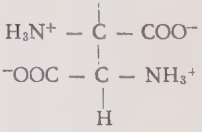


Strongly acid in aqueous solution.[1]

The so-called "inner salts" include substances which are practically non-electrolytes and whose dissociation constant is about $K = 10^{-10}$, as well as conductors which have decided acid properties and are at least as strong as formic acid ($K = 10^{-4}$ and higher). In view of these facts, differentiations on the basis of constitution must also be made. The name and conception "salt = electrolyte" as defined by Hittorf is as little applicable to such aliphatic, non-conducting "amino acids[2] and betaines," as it is to the non-conducting "inner complex salts."

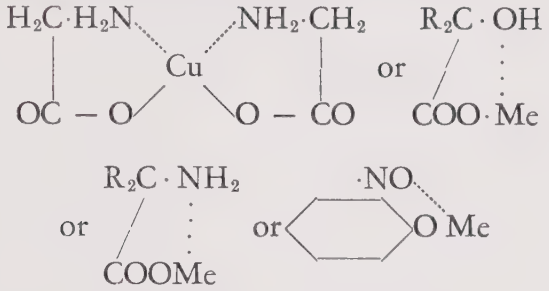
[1] Hantzsch, Z. Elektrochem., **29**, 230 (1923).

[2] It may be mentioned that the diamino-succinic acids meso-, (d, l), d- and l- forms): may be regarded as special type of "bi-dipolar" compounds.



Inner Metallic Complex Salts.

Through the investigations of Ley[1] and Bruni[2] this group of metallic salts, beginning with a study of copper glycocoll, has assumed a position of prominence in scientific interest. Ley was the first to create the term "inner complex salts" and to give a structural formula to such compounds. The metallic atom in such a compound is linked both by principal and secondary valences to the various components of the molecule, thus—



Consequently the metallic atom is much more firmly bound and shows different properties. The salt possesses an unusual color, is very appreciably soluble in organic solvents, shows a very slight conductivity and an anomalous analytical behavior. The metallic atom is not at all or only to a slight degree present in the ionic form.[3]

These compounds can hardly be called salts, if we apply the criteria for electrolyte-salts set up by Hittorf, namely, pronounced conductivity and reactivity, as well as mutual interchange of ions. Thus copper glycocoll at 25° in aqueous solution[4] has the conductivities, λ_{25},

v	= 32	64	128
λ_{25}	= 0.20	0.38	0.52

or cobalt glycocoll v = 33, λ_{25} = 0.6.

[1] Z. Elektrochem., 10, 954 (1904).
[2] Atti accad. Lincei, [2] 13, 26 (1904).
[3] Ley, Ber., 57, 1707 (1924).
[4] It is a curious fact that aqueous solutions of copper glycocoll are intensely dark blue. For other values and data on light absorption of these salts, see Ley, Z. anorg. Chem., 164, 386 (1927).

In this respect the "inner complex salts" may be classed with the so-called non-conducting complex metal ammonium salts of Werner, such as the cobalt-triammine $Co(NH_3)_3(NO_2)_3$, platinum diammine, and chromium triaquo salts. Even in the case of these "non-conductors" (that is, non-conductors according to Werner's theory) the idea "salt = electrolyte" is not properly applicable in its most limited sense. Both classes of substances behave as poor electrolytes, but not as salts. It is much more logical to consider them as neutral organic metallic, or complex metallic compounds, possessing the character of homeopolar (organic) compounds.

Abnormal Electrolytes (Walden); *Auto-Ionization of Solvents*

Having found liquid sulphur dioxide to be a good ionizing solvent for various inorganic salts, and the halides of the ammonium bases, Walden undertook to measure the conductivity of solutions of a series of compounds which were not of the *salt* type as judged by their behavior in aqueous solution. In addition to sulphur dioxide, such substances as arsenic trichloride and sulfuryl chloride were also employed as ionizing solvents. The compounds which were investigated with reference to their conductivity and ionic dissociation included:—

I. The free halogens bromine and iodine.

II. Certain interhalogens such as ClI and BrI.

III. Halides of phosphorus, arsenic, antimony, tin, and sulphur.

IV. Tertiary nitrogen bases; dimethyl pyrone; carbinoles.

V. Hydrocarbons and their halide derivatives.

VI. Acyl chlorides and bromides.

Since solutions of these substances in one or more of the above solvents, in the majority of cases showed a measurable conductivity, Walden called this whole group of compounds "abnormal electrolytes," and undertook to determine their ions theoretically.[1] Although these measure-

[1] Ber., 32, 2862 (1899); 35, 171 (1902); Z. physik. Chem., 39, 513 (1902); 43, 385 (1903).

ments had to do with the behavior of these substances in non-aqueous solvents, Walden[1] had previously observed such abnormal electrolytes in aqueous solution. In the latter case the investigations dealt with organic "non-conductors," such as Kiliani's saccharine, iso-saccharine, esters of malonic, aceto-acetic, cyan-acetic and *o*-nitro-benzoyl malonic acids (the ester was a strong acid), and their respective sodium compounds. All these "non-electrolytes" were found to be "abnormal electrolytes" since they showed a measurable, and sometimes an appreciable conductivity. Acid imides (succinimide), acid amides (asparagine) and dimethyl maleic acid anhydride, were also studied with reference to their electrolytic nature.

Investigations by Walden[2] on the conductivity of *pure solvents* and ionizing media, and their "auto-ionization," subsequently began to appear at regular intervals.

These studies led to two important conclusions:—(1) that carefully purified solvents possessed a measurable conductivity which could serve as a diagnostic aid in the differentiation of ionizing solvents; and (2) that this residual conductance was due "to the electrolytic dissociation of the pure solvent itself." Assuming this "self-ionization" or "auto-ionization" to take place, a series of postulations as to the "nature of the ions" was made. These are presented in Table I.

These investigations were of fundamental importance for several reasons, first, because they pointed very definitely to the self-conductance and "auto-ionization" of solvents, and consequently directed attention to the large class of "abnormal" electrolytes which had previously been designated as non-electrolytes; and secondly, because they brought out the relationship between the auto-ionization of non-aqueous solvents and the tendency towards ionization of dissolved substances.

[1] Ber., **24**, 2025 (1891); J. Russ. Phys. Chem. Soc., 1891.

[2] Z. anorg. Chem., **25**, 209 (1900); **29**, 371 (1902); Bull. acad. sci. St. Petersburg, June 1901. Concerning organic solvents see Z. anorg. Chem., **30**, 145 (1902); and for organic ionizing solvents see Z. physik. Chem., **46**, 103 (1903).

Similar views were expressed by Lewis and Wheeler[1] who say "that those liquids which in the pure state are the best conductors of electricity, are also the best dissociating

TABLE I

Auto-Ionization of Pure Solvents

I. Inorganic Solvents	II. Organic Solvents
$SO_2 = SO^{++}$ and S^{++}	alcohols, $ROH = RO^- + H^+ \leftrightarrows R^+ + OH^-$
$POCl_3 = PO^{+++} + P^{+++}$	aldehydes, $RCOH = RCO^- + H^+$ (or $RCH^{++} + O^{--}$)
$AsX_3 = AS^{+++}$	acid anhydrides, $(RCO)_2O = 2RCO^+ + O^{--}$
$SbX_3 = Sb^{+++}$	acyl halides, $RCOX = RCO^+ + X^-$
$NH_3 = NH_2^- + H^+$	ester, $RCOOR = RCOO^- + R^+$ (or, $RCO^+ + OR^-$)
$SOCl_2 = SO^{++}$	acid amides, $RCONH_2 = RCO^+ + NH_2^-$
$SO_2Cl_2 = SO_2^{++}$ and $ClSO_3H = ClSO_3^-$	nitriles, $RCN = R^+ + CN^-$, or acetonitrile, $CH_3CN = (CNCH_2)^- + H^+$
$H_2SO_4 = HSO_4^-$	thiocyanates, $RCNS = R^+ + NSC^-$
$SO_2(OCH_3)_2 = SO_2OCH_3O^- + CH_3^+$	nitro compounds $CH_3NO_2 = CH_2^-NO_2 + H^+$ or $CH_3^+ + NO_2^-$

agents when acting as solvents." Substances of this kind are termed "electrophiles" by them. With the development of the electronic theory, Lewis[2] classes electrophiles or ionizing solvents with the "polar type" compounds.

[1] Z. physik. Chem., **56**, 188 (1906).
[2] J. Am. Chem. Soc., **38**, 762 (1916).

True Salts in Solid State.

True salts, typical heteropolar substances corresponding to sodium chloride, have been found by X-ray studies to possess ionic lattices in the solid state. According to Reis[1] there is a decided difference between the structure of ionic and molecular lattices. In the former the points in the crystal lattice are occupied by ions; in the latter by self-existent, individual molecules. Strong electrostatic forces are active between the ions of the former. Consequently they form very stable structures which are disturbed only with difficulty. Such compounds are characterized by high melting and boiling points, and by their slight solubility in organic solvents. The weak molecular forces of organic solvents (as indicated by their dielectric constants, which are usually very much less than that of water) are evidently incapable of overcoming the powerful electrostatic attraction between the ions in the lattice structure. Kossel[2] differentiates in somewhat the same way, between difficultly fusible substances having ionic lattices and easily fusible substances with molecular lattices. Opposing forces within the ionic lattices of the former, in which the "material particles are to a certain extent interlocked", are believed to exercise a profound effect.

On the basis of similar deliberations W. Biltz[3] classes the volatile halides of aluminum with the autocomplex salts and non-electrolytes, rather than with the salts. Pfeiffer,[4] on the other hand, assigns a dipolar formula to the non-volatile organic amino-acids and betaines ("inner salts").

The question may indeed be asked: What substances possess polar linkage, that is, belong to the class of true, heteropolar salts? Grimm gives the following answer: "The only substances which so far approach *ideal polar linkage* that they can with certainty be regarded as polar, are the compounds of the alkalies and alkaline

[1] Z. Physik, 1, 204 (1920).
[2] Ibid., 1, 395 (1920).
[3] Z. physik. Chem., 100, 63 (1922).
[4] Ber., 55, 1763 (1922).

earths with the halogens, oxygen, sulphur, selenium and tellurium. They correspond to NaCl..., Na_2S, $MgCl_2$ and MgS. Double salts and mixed crystals of these substances may naturally also be put in this class. . . . Even the metallic hydrides possess the character of salts of polar structure."[1] It is worth noting that, by the above criterion, the number of true salts is very small, and is limited to the simplest binary compounds.[2]

IN RETROSPECT CONCERNING "SALTS"

True salts are therefore compounds whose outstanding properties include crystalline form, crystal lattice (ionic lattice), solubility in water, difficult solubility in non-aqueous solvents, and difficult fusibility. Let us compare these modern characteristics of a salt with those ascribed to this class of compounds a hundred or more years ago. The definition given by Cavallo in 1781 runs: "Salts or salty substances are those bodies which dissolve in water, have taste, and lie intermediate between water and the purest earths with respect to their weight and ability to withstand fire."[3]

Twenty-five years later in Klaproth's revised edition[4] of Gren's "Handbuch der gesammten Chemie," salts are characterized by their solubility in water, such that "not more than two hundred parts of boiling water are necessary to dissolve one part of salt. They excite a taste on the tongue, and form crystals." Taste, solubility in water, crystal form, "resistibility to heat and volatility, and behavior towards other substances" are especially emphasized as points of distinction for "neutral" (alkali) salts. The same is true of "intermediate (alkaline earth) salts" or "earthy intermediate salts." The *salia metallica* or "intermediate salts with metallic bases" (heavy-metal salts), are again to be differentiated by "their ability to

[1] Similar views are expressed by Madelung, Ann., 427, 35 (1922). See also Hantzsch and Carlsohn, Z. anorg. Chem., 160, 15 (1927).

[2] See Faraday's views on electrolytes.

[3] Cavallo, *Abhandlung über die Natur und Eigenschaften der Luft*, p. 30 ff (German transl., Leipzig, 1783).

[4] Parts I and II (1806); Part III (1807).

crystallize, by their crystal form, behavior towards fire and air, solubility in water and alcohol, and by their taste."

It is plain to see from these quotations that the readily determinable conditions of state (crystallization, crystal structure, behavior towards water, alcohol and heat, as well as taste) serve as criteria for the differentiation of the alkali, alkaline earth, and metallic salts. Are not these fundamentally the same properties which we meet today in connection with ions and electrostatic forces?

Let us discuss next the process of *solution* of an electrolyte. Hantzsch's[1] statement is probably the most definite expression of modern opinion with reference to the chemistry of this process. Thus when alkali halides, which crystallize in ionic lattices, dissolve in water "the metal and halogen ions, existing within the crystal lattice and completely saturated chemically with respect to one another, possess in addition partial or residual valences on their outer surface. Consequently they may react on contact with the "di-pole" water in such manner that the hydrogen atom of the latter attaches itself to the halogen atom, and the oxygen to the metallic atom, resulting in the formation successively of the monohydrate, Me$\overset{OH_2}{\diagdown\!\!\diagup}$X, then the dihydrate Me$\overset{OH_2}{\underset{OH_2}{\diagdown\!\!\diagup}}$X, etc." This process of hydration could be formulated just as well if we assumed the addition of the dipole, water, to each individual ion

$$Me^+ \!-\!- X^-$$

$$\left(\begin{matrix}\vdots\\ OH^-\\ |\\ H^+\end{matrix}\right)\left(\begin{matrix}\vdots\\ H^+\\ |\\ OH^-\end{matrix}\right)$$

The symbolization Me$\overset{OH_2}{\diagdown\!\!\diagup}$X could be given still

[1] Ber., 59, 1103 (1926). See also Fajans.

another form by simply omitting the letters and leaving only the characteristic electric charges: $\begin{matrix} \oplus - \ominus \text{ (salt)} \\ \ominus - \oplus \text{ (water)} \end{matrix}$ This idea of a "polarization" or attachment, by virtue of electrostatic forces, of water molecules to those of the electrolyte is not a new one and can be found in many of the older writings.

In pointing out the peculiar manner in which ionization is promoted by the use of water as a solvent, Ciamician[1] arrives at the following molecular-kinetic deductions[2] concerning the electrolytic dissociation of salts, acids, and bases: "One may assume, when salt and water particles meet, that the oxygen and hydrogen atoms of the latter exert an attraction upon the cation and anion, respectively, of the salt, which may eventually bring about separation into ions. This implies no decomposition of the water molecules. They surround the free ions as if they were in a polarized condition. Presumably they arrange themselves so that the oxygen atoms lie towards the metal atoms, and the hydrogen atoms toward the negative radical. Reaction of water with the ions is prevented by the electric charges which arise as soon as separation into ions takes place, since each ion becomes the bearer of an equal but opposite quantity of electricity. Whatever applies to salts holds also for acids and bases, as the rôle of water may in these cases be explained in the same way."

Worthy of attention in this statement are the suggestions that the water "dipoles" then arrange themselves in a definite position with respect to the ions, surround the latter, and remove them from the sphere of electrostatic attraction.

Let us go back still further into the past. Using sodium chloride as an example Grotthuss[3] (1819) pictured the act of solution as follows: "The process of solution of a salt

[1] Z. physik. Chem., **6**, 403 ff. (1890).

[2] These deductions were the result of a correspondence carried on between Ciamician and W. Ostwald.

[3] "Über die chemische Wirksamkeit des Lichtes und der Elektrizität," see Ostwald's *Klassiker*, No. **152**, 116.

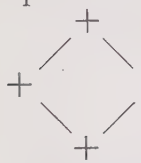
in water apparently consists either of an interpolation of its own elementary particles into the perpetually active galvanic circle of molecules of water, or a joining of the elements of the salt with the galvanic molecular activity of water. Salts incapable of doing either are called insoluble. This action doubtlessly raises the galvanic molecular activity of water so that its electrical conductivity is increased.[1] If common salt in the dry state be considered, in accordance with the views of Gay-Lussac, Thénard, and Davy, as "chlorine natronium," and if chlorine be represented by − and natronium by +, the combination of one atom of the salt with one of water may be depicted as $\begin{matrix} - & + \\ + & - \end{matrix} \begin{matrix} (Cl & - & Na) \\ (H & - & O) \end{matrix}$ this results in the formation of a circular galvanic molecular movement, as mentioned before."

As early as 1805, Grotthuss, in the *first* theory of electrolysis, represented water as a polar structure between hydrogen, designated as +, and oxygen as −, by the symbol +−. Except for the somewhat antiquated method of expression, his explanation of the process of solution of a salt in water is quite similar to that which the modern electrochemist and physical chemist would give today. Water is not to be regarded as an indifferent solvent and diluent of salt particles; it is an active substance, a polar compound (dipole) which, by virtue of opposing electrical forces, may (1) attach itself to salt ions, or (2) enter into the salt molecule to cause a loosening of the electrostatic bonds in the salt molecule and bring about a rise in the conductivity of the solution.

Grotthuss' views on the "ever present polar molecular activity of water," and the "elementary polar circle" are indeed a bold anticipation of the later theories on tautomerism, dissociation and dipolar activity. He says:

[1] The assumption is here that water primarily undergoes electrolysis, and that the presence of the salt, acid or base only facilitates conduction. This view was at first accepted by Faraday, but not by Hittorf. Werner subsequently advanced his theory in which the primary rôle of water was emphasized. Recently Doumer and Palmaer have defended the theory of primary decomposition. Verschaffelt not long ago emphasized the correctness of this idea from the standpoint of modern theories. (C. A., **21**, 1585 (1927); see also E. Doumer, Compt. rend., **184**, 747 (1927).

"Since the elementary particles of a . . . liquid are attracted and repelled by other elementary particles lying all around it, it is entirely possible that a continuous *exchange* of heterogeneous elements, such as might be depicted by an 'elementary polar circle' such as this



, may take place."[1]

According to Berzelius, those substances which travel to the positive pole are acids, while those which go to the negative pole are bases. Both acids and bases are regarded as oxides. Grotthuss (1818) showed to the contrary "that there can be no acid that is not electropositive toward another, still stronger acid (that is, as a base); likewise there is no base that would not become electronegative (that is, an acid) towards another, more powerful one."[2,3] Grotthuss regards the terms "acid" and "base" as relative,[4] and he was therefore, one of the first to realize their amphoteric character. He continues—"From this point of view there would be no one definite acid except oxygen, the most electronegative of all, nor would there be any well-defined base except hydrogen, which is the most electropositive of all bodies." This brings us back to the old idea of primal acid and primal base.[5] "But," says Grotthuss, "neither is oxygen by itself acidic, nor is hydrogen by itself basic or alkaline. Such a theory would therefore compel us to regard as the absolute

[1] *Ibid.*, p. 161, 167. Comp. also the views of Hittorf and Arrhenius.

[2] Ostwald's *Klassiker*, No. **152**, p. 90.

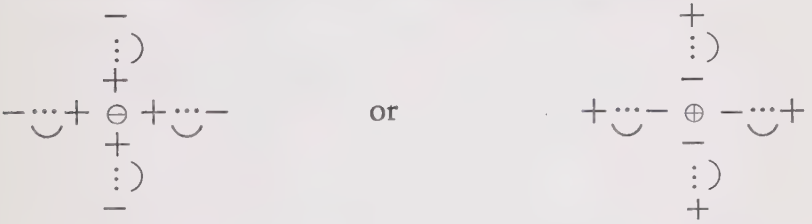
[3] This conjecture, original with Grotthuss, was subsequently verified. His ideas bring to mind the investigations of Wolcott Gibbs, who synthesized the complex acids of phosphorus, arsenic, tungsten and molybdenum, as well as those of Edgar F. Smith, Werner, Miolati, Rosenheim and others, who created the chemistry of the hetero- and poly-acids. Concerning the hetero-poly acids, Werner says (Neuere Anschauungen etc. 4th Edition p. 146, 125, 282 (1920)) that "the individual components have different electro-chemical properties and metallo-acids may accordingly act as bases towards metalloid acids." In the converse case, where "Base A" combines with "Base B" to form a "hydroxo salt," the salt formation is due to association of the basic metallic hydroxides, *e. g.* $Zn(OH)_2 + KOH = [Zn(OH)_3]K$

[4] Compare the views of Avogadro, Gay-Lussac, and Oersted.

[5] See Tachenius, Lemery, Cavallo (1781).

acid only one substance, namely oxygen, which has no acid properties, and as absolute base, or absolute alkali, only one substance which is not in the least alkaline."

With these anomalies in mind he then calls attention to his own definition of acid and base in which he points out the important part played by water as a solvent.[1] It involves his theory of the "polar disposition" of the elementary particles of water in the circuit, where the oxygen turns to the positive pole and the hydrogen to the negative pole. "If acids, that is, electronegative bodies, come in contact with water, or are dissolved in the latter, it is quite probable that the elements of water arrange themselves so that hydrogen is turned towards the acid, and the oxygen away from it. . . . Exactly the opposite must take place in potash solutions. Here the oxygen must be oriented towards the electropositive potassium, while the hydrogen of the water must be turned away from the latter."[2] If potash solutions or a cation be represented by ⊕, acids or an anion by ⊖, and water by the "dipole" $+\cdots-$ then conditions can be expressed symbolically as



The electrostatic significance of ion hydration is today depicted in the same way. In the neighborhood of an ion the water molecules, as dipoles, are under the influence of the electric field, so oriented or polarized that the opposite pole turns towards the ion, the like one away from it.

[1] See Schweigger's Journ. f. Chemie u. Physik., 9, 331 (1814).
[2] Compare Ostwald's *Klassiker*, No. 152, p. 150.

CHAPTER VI.

The Latest Phase in the Development of the Concept "Acid-Base"

Lowry proposes the following formulation:—

"A *base* is an acceptor for the hydrogen nucleus, that is the proton, as $NH_3 + H^+ = NH_4^+$.

"An *acid* is a hydride from which a proton can be detached, *e.g.* upon dissolution in an ionizing solvent, on electrolysis, or by displacement by a metallic ion."[1]

The inner mechanism of ionization is, accordingly, not assumed to be a simple dissociation in the sense of the equations:

$$HCl \leftrightarrows H^+ + Cl^- \quad \text{or} \quad HCl\ aq \leftrightarrows H^+aq + Cl^-aq$$

but a more complex reaction:

$$HCl + OH_2 \leftrightarrows OH_3^+ + Cl^-,$$

$$\text{or} \quad NH_3 + HCl \leftrightarrows NH_4^+ + Cl^-$$

If the proton in aqueous solutions is assumed to be hydrated, its formula may be expressed as OH_3^+. The reaction of NH_3 can then be written: $NH_3 + OH_3^+ \leftrightarrows NH_3.OH_3^+$. Of great import in this definition is the fact that the old basis of the hydrogen theory of acids is retained, namely, that hydrogen is considered as the element which is absolutely necessary for the characterization of acids and bases. This element is at the same time reclothed in modern theoretical habiliments.

Similar ideas were advanced simultaneously by various investigators. In this connection particular reference should be made to the considerations and studies of Brönsted.[2] If, as in the case of ammonia, the arrangement

$$NH_4^+ + OH^- \leftrightarrows NH_4OH$$

is assumed to be general for the characterization of bases

[1] Chemistry and Industry, **42**, 43 (1923); Trans. Faraday Soc., **20**, Pt. I, no. 58 (1924).
[2] Rec. trav. chim., **42**, 718 (1923).

"one would be forced to introduce a different definition for a base for each and every solvent. The acidic and basic properties are, however, fundamentally independent of the nature of the solvent." Brönsted presents the following formulation as independent of the nature of any chosen solvent: "Acids and bases are substances capable of splitting off or adding on hydrogen ions:

$$S \leftrightarrows B + H^+ \text{ "}$$

acid base

concentration a_S a_B a_{H^+}

Brönsted[1] calls this property of association of hydrogen ions "hydriophilie." He says further that "it is typical of bases, and all substances capable of it are to be designated as bases." "As illustrated by the following scheme

$$NH_3 + H^+ \leftrightarrows NH_4^+$$
$$\updownarrow$$
$$NH_4OH$$

ammonia could be called the true[2] base, whereas ammonium hydroxide would be termed the pseudo-base. This would correspond to the assumption that ammonium hydroxide is incapable of adding on hydrogen ions."

In accordance with this definition only the so-called anhydro-bases, such as ammonia, aniline, benzylamine, can be considered as true bases. The expression

$$K_S = \frac{a_B \cdot a_{H^+}}{a_S}$$

is designated by Brönsted and Pedersen[3] as the dissociation or acid constant, K_S, whereas its reciprocal

$$K_B = \frac{a_S}{a_B \cdot a_{H^+}}$$

is called the association or base constant, K_B. This conception has led Stewart and Aston[4] to assume that "the

[1] Z. physik. Chem., 108, 192 (1924).
[2] Compare the term "true base" as used here with the definition given in Werner's theory.
[3] Z. physik. Chem., 108, 230 (1924).
[4] J. Am. Chem. Soc., 48, 1643 (1926).

formation of a salt of an amine may be considered as simply the addition of a hydrogen ion to the unoccupied pair of electrons on the nitrogen atom:

$$R_3N: + H^+ \leftrightarrows R_3N^+:H''$$

Although water is only one of many solvents, it is the best known, and it has been studied more exhaustively than any other one. The behavior of various substances towards water as a solvent has led: (1) to their classification, (2) to the determination of their constitution, and (3) to the development of new theories. It is not only permissible, but even necessary to include in these theoretical considerations other solvents whose use leads to new lines of experimental attack. It has been said, "We think in relations." What relationships, and what analogies between water on the one hand and ammonia, for instance, on the other, may be deduced for the "theory of cognition?"

Franklin's Ammono-System of Acids, Bases and Salts.

Using the criteria which have characterized water as the ionizing solvent of the oxygen system of acids, bases, and salts, Franklin[1] has applied them in a very discerning manner to the peculiar solvent ammonia. From them he has evolved his theory of "*ammono*-bases," "ammono-acids," and "ammono-salts."

If the hydrogen atom in water be replaced by a metallic atom or by a negative element or radical, bases MeOH, acids $HO{\cdot}NO_2$ or HOX, and salts $MeO{\cdot}NO_2$ or MeOX, may be regarded as structural derivatives of water. If these substitution products be called *aquo*-base,[2] aquo-acid, and aquo-salt, respectively, then a corresponding system of *thio*-bases, -acids and -salts may be derived from hydrogen sulphide, HSH. In a similar manner a series of compounds may be derived from ammonia, HNH_2, which bear the same relationship to it as aquo-compounds do to water.

[1] J. Am. Chem. Soc., **46**, 2137 (1924); **27**, 820 (1905). Also Am. Chem. I., **47**, 285 (1912).

[2] These terms have a different significance in Werner's theory.

AMMONO-BASES

Parallel reactions:

$$K + HOH = K(OH) + H \text{ (in water)}$$
$$K + HNH_2 = K(NH_2) + H \text{ (in ammonia)}$$
$$AgNO_3 + KOH = Ag(OH) + KNO_3 \text{ (in water)}$$
$$AgNO_3 + KNH_2 = Ag(NH_2) + KNO_3 \text{ in ammonia)}$$

and so on.

A solution of phenolphthalein in liquid ammonia is colorless. The addition of a few drops of a solution of potassium amide in ammonia immediately causes the solution to turn red. If now a few drops of dicyanimide $(CN)_2NH$ are added, the solution is promptly decolorized. Solutions of potassium amide, cyanamide, dicyanimide and their salts in liquid ammonia, conduct the electric current.

AMMONO-ACIDS

of the Third Group:

$B(NH_2)_3$ analogous to $B(OH)_3$
$B_2(NH)_3$ analogous to B_2O_3
$HN = Al-NH_2$ analogous to $OAl(OH)$,

of the Fourth Group:

$C(NH_2)_4$	$HN{\cdot}C(NH_2)_2$	$NC{\cdot}NH_2$	$(NC)_2NH$	C_3N_4
$Si(NH_2)_4$	$HN{\cdot}Si(NH_2)_2$	$NSi{\cdot}NH_2$	$(NSi)_2NH$	Si_3N_4
$Ti(NH_2)_4$	——	$NTi{\cdot}NH_2$	——	Ti_3N_4
$Sn(NH_2)_4$	——	$NSn{\cdot}NH_2$	——	——

(of the type $OC(OH)_2$)
(of the type $C(OH)_4$)

of the Fifth Group:

$N(NH_2)_5 \rightarrow HN=N(NH_2)_3 \rightarrow N\equiv N(NH_2)_2 \rightarrow N\equiv N=NH$ (hydronitric acid),
analogous to $N(OH)_5 \rightarrow ON(OH)_3 \rightarrow O_2NOH$.

Hydrogen cyanide, HNC, is structurally an ammonocarbonous acid. The formula represents this acid as am-

monia, HNH_2, in which two of the hydrogen atoms have been replaced by a negative divalent carbon atom,

$$HN(H_2) \rightarrow H{\cdot}N{:}C$$

Hydronitric acid (azoimide, hydrazoic acid), HN_3, first isolated by Curtius, is represented as a deammonation product of ortho-ammono-nitric acid,

$$HN=N\begin{matrix}\diagup NH_2 \\ -NH_2 \\ \diagdown NH_2\end{matrix} - 2NH_3 \rightarrow HN=N\equiv N$$

Numerous reactions support this conception. Thus, a mixture of hydrochloric and hydronitric acid dissolve gold and platinum and oxidize ferrous iron to the ferric state. If a mixture of hydronitric and hydriodic acids is warmed, iodine is liberated. The same mixture dissolves gold very rapidly. Potassium nitrate reacts in liquid ammonia with potassium amide to give potassium azide:

$$KONO_2 + 2NH_3 \rightarrow K.N{:}N{:}N + 3H_2O$$

A. W. Browne and his co-workers[1] have developed a system of acids, bases and salts from hydrazine, which is comparable in scope and character with water and ammonia.

In the absence of any solvent and in the vapor state (at 250-350°), ammonium chloride is regarded as a peculiar form of hydracid by K. A. Hofmann.[2] If dry sal ammoniac vapor is allowed to act upon copper, nickel, silver, or iron, a far more energetic evolution of hydrogen takes place than is the case when these metals are acted upon by an equivalent quantity of hydrogen chloride. The reaction which takes place is a replacement of hydrogen by metal in the ammonium complex:

$$Me + (NH_4)Cl = (NH_3Me)Cl + H$$

analogous to the action of concentrated hydrochloric acid:[3]

$$Me + (OH_3)Cl = (OH_2Me)Cl + H$$

[1] J. Am. Chem. Soc., **37**, 497, 816, 825 (1915); **48**, 682 (1926).

[2] With Hartmann and Nagel, Ber., **58**, 808 (1925).

[3] The fact must not be overlooked that, under the conditions of the experiment (absence of water and in the vapor phase) the reactions taking place are not, or need not necessarily be, ionic in nature, whereas the hydrogen ion or its hydrate do take part when aqueous hydrochloric acid is employed.

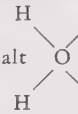
Hofmann concludes: "Dry sal ammoniac is an ammonium acid; concentrated aqueous hydrochloric acid is a hydroxonium acid." Sal ammoniac, however, may be considered formally as an ammonia interposition product[1] of hydrogen chloride, $HCl + NH_3 = H(NH_3)Cl$. The action on metals may therefore be expressed:

$$H(NH_3)Cl + Me = Me(NH_3)Cl + H$$

RECENT THEORETICAL VIEWS ON "ACIDS" AND "BASES"

The modern views on valence and structure of atoms have also influenced the conceptions of "acids" and "bases." G. N. Lewis, in his excellent book "Valence and the Structure of Atoms and Molecules,"[2] says, "When we discuss aqueous solutions of substances which do not contain hydroxyl, it is simplest to define a base as a substance which adds hydrogen ion. Thus, ammonia adds hydrogen ion to form ammonium ion, and the degree to which this occurs will vary as we substitute other radicals for hydrogen. Indeed, if we wish, we may consider ammonium ion as an acid and say that its strength as an acid is increased when hydrogen is replaced by Cl or OH or NH_2. This is precisely the same as saying that ammonia is a weaker base when such substitutions are made."

"Since hydrogen is a constituent of most of our electrolytic solvents, the definition of an acid or base as a substance which gives up or takes up hydrogen ion would be more general than the one that we used before, but it will not be universal."[3]

[1] Since the action between both gases is dependent upon traces of water, and since we admit that HCl forms an oxonium salt  or $H(H_2O)Cl$ with water, the formation of sal ammoniac can be considered as a displacement reaction:

$$H(H_2O)Cl + NH_3 \rightarrow H(NH_3)Cl + H_2O.$$

[2] Am. Chem. Soc. Monogr., —, 141ff. (1923); German ed., Naturwissenschaften, 77, 158 (1927).

[3] Compare the views of Bredig, A. Werner, Lowry and Brönsted.

"Another definition of an acid and a base in any given solvent would be the following: An acid is a substance which gives off the cation or combines with the anion of the solvent;[1] a base is a substance which gives off the anion or combines with the cation of the solvent."

Let us apply some of these rules and definitions to actual cases.

First: to *acids*,

(a) Where acid and solvent give off the same cation:

HBr in H_2O $(= H^+ + OH^-)$: $HBr \rightarrow H^+ + Br^-$

HBr in NH_3 $(= H^+ + NH_2^-)$: $HBr \rightarrow H^+ + Br^-$

HBr in CH_3COOH $(= H^+ + CH_3COO^-)$: $HBr \rightarrow H^+ + Br^-$

(b) Combination with the anion of the solvent:

$$BCl_3 + H_2O\ (= H^+ + OH^-) \rightarrow (BCl_3 \cdot OH)^- + H^+$$

$$BCl_3 + NH_3\ (= H^+ + NH_2^-) \rightarrow (BCl_3 \cdot NH_2)^- + H^+$$

$$BCl_3 + CH_3COOH\ (= CH_3COO^- + H^+) \rightarrow (BCl_3 \cdot CH_3COO)^- + H^+$$

However, according to Lewis' definition, an addition of the solvent anion might also be postulated for HBr, HCl, etc., thus

in H_2O $(= H^+ + OH^-)$: $OH^- + HBr = H_2OBr^-$

in NH_3 $(= H^+ + NH_2^-)$: $NH_2^- + HBr = H_3NBr^-$

in CH_3COOH $(= CH_3COO^- + H^+)$: $CH_3COO^- + HBr = (CH_3COO\ HBr)^-$

in CH_3OH $(= CH_3O^- + H^+)$: $CH_3O^- + HBr = (CH_3OHBr)^-$

This would result in the formation of rather distinctive anions, which could be regarded formally as solvated halogen ions. In these instances the hydrogen ion is retained as the characteristic element of all acids. It is present in solution, derivable either from the solute (HX) or from the solvent (H_2O, NH_3, CH_3OH, RCOOH).

[1] In this connection the idea of "auto-ionization" of a solvent enters as a tacit and logical assumption. See discussion of "abnormal electrolytes" *see* p. 136.

Second: to *bases*,

(a) Formation of an anion similar to that of the solvent:
$NaOH + H_2O\ (= H^+ + OH^-) \rightarrow Na^+ + OH^-$ (or by combination with the cation: $NaOH + H^+ = (NaOH_2)^+$)
$N(C_3H_7)_4OH\ (+ H_2O) = N(C_3H_7)_4^+ + OH^-$
(or $N(C_3H_7)_4OH + H^+ = (N(C_3H_7)_4\ OH_2)^+$)
$NaNH_2 + NH_3\ (= H^+ + NH_2^-) = Na^+ + NH_2^-$
(or $NaNH_2 + H^+ = (NaNH_3)^+$)

Let us take the case of methyl alcohol, CH_3OH ($= CH_3O^- + H^+$) and $NaOCH_3$ ($= Na^+ + {}^-OCH_3$). We have $CH_3ONa + CH_3OH \rightarrow CH_3O^- + Na^+$. Again NaOH is also an electrolyte in methyl alcohol, $NaOH \rightleftarrows Na^+ + {}^-OH$. But sodium hydroxide is also a basic electrolyte in methyl alcohol (that is, it yields hydroxyl ions); consequently we would have to assume that methyl alcohol may also dissociate into CH_3^+ and OH^- ions. Methyl alcohol would therefore seem to be an "amphoteric" electrolyte.

It will be noted that the same anion, CH_3COO^-, is assumed to be present in a solution of potassium acetate in acetic acid. The salt CH_3COOK would therefore have to be regarded formally as a "base". Likewise, potassium nitrate would have to be termed a base when dissolved in nitric acid. If potassium chloride is dissolved in antimony trichloride, the anion of the solvent will again be similar to that of the salt. The latter would therefore again be a "base." Hydrogen chloride in antimony trichloride would also be a "base," since it yields the same anion as the solvent. If we assume that hydrogen chloride or potassium chloride unites with the anion of this solvent, $SbCl_3$ ($= SbCl_2^+ + Cl^-$), each would then appear to be an "acid"

$$HCl + SbCl_2^+ + Cl^- \rightarrow HCl{\cdot}Cl^- + SbCl_2^+,$$
or $$KCl + SbCl_2^+ + Cl^- \rightarrow KCl_2^- + SbCl_2^+.$$

Conversely, if antimony trichloride is dissolved in liquid hydrogen chloride, both dissociate to give the same anion, thus making antimony trichloride a "base." Should it add the Cl^- anion, it would have to be regarded as an "acid" ($SbCl_3 + Cl^-$).

(b) Combination with the cation of the solvent:

$C_6H_5NH_2 + H_2O\,(= H^+ + OH^-) = (C_6H_5NH_2{\cdot}H^+) + OH^-$
$C_6H_5NH_2 + NH_3\,(= H^+ + NH_2^-) = (C_6H_5NH_3{\cdot}H^+) + NH_2^-$
$C_6H_5NH_2 + CH_3COOH\,(= H^+ + CH_3COO^-) =$
$(C_6H_5NH_2.H^+) + CH_3COO^-$
$KNH_2 + NH_3\,(= H^+ + NH_2^-) = KNH_2{\cdot}H^+ + NH_2^-$

The hydroxyl ion, heretofore assumed to be the characteristic basic group, is present in only a few of the cases discussed above.

Let us consider ammonia in connection with liquid hydrogen bromide as solvent.

$$NH_3(= NH_2^- + H^+) \text{ and } HBr\,(= H^+ + Br^-).$$

Since both give off the same cation, H^+, ammonia may be regarded as an "acid." But since combination with the cation of the solvent is possible ($NH_3 + H^+ = NH_4^+$), ammonia may be regarded as a "base."

Or let us consider a *typical* "salt" such as potassium iodide. Since this substance acts as an electrolyte in molten iodine, several assumptions are permissible. Iodine as a solvent dissociates in accordance with the equation

$$I_2 \leftrightarrows I^+ + I^-$$

Potassium iodide ionizes as $KI \leftrightarrows K^+ + I^-$. Since both substances contain the same anion, potassium iodide may be called a "base." The alkali iodides are known to combine with iodine to form polyiodides. If now the cation I^+ is added, a rather uncommon complex ion $(KI{\cdot}I)^+$ would result! Likewise, the addition of the solvent anion I^- would give the complex anion $KI{\cdot}I^-$. In the latter case we would be forced to call potassium iodide an "acid." A similar series of deductions are possible when potassium iodide is dissolved in hydrogen iodide.

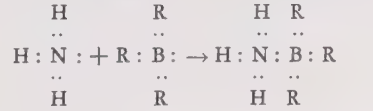
However, Lewis gives an even wider meaning to his definition when he says: "Even this broad definition is not entirely satisfactory. We are inclined to think of substances as possessing acid or basic properties, without having a particular solvent in mind. It seems to me that with complete generality we may say that a basic substance is one

which has a lone pair[1] of electrons which may be used to complete the stable group of another atom, and that an acid substance is one which can employ a lone pair from another molecule in completing the stable group of one of its own atoms. In other words, the basic substance furnishes a pair of electrons for a chemical bond, the acid substances accept such a pair."

In this definition of "acid" and "base," every reference to, and all dependency upon characteristic ionic types is eliminated. Neither hydrogen nor hydroxyl ions act as a "*conditio sine qua non*" for acid and basic properties. Dissociation constants of "acids" and "bases" therefore become meaningless, and the numerical data of conductivity play a minor rôle. Criteria for formation of neutral salts, as well as oppositeness of acids and bases with reference to certain color indicators, would appear to have been purely incidental observations. Typical binary salts become "acids" or bases." The important chemical part played by the solvent in the "development" and the "appearance" of acid and basic properties is purposely eliminated. The new hypothetical conception of the "lone pair of electrons" is to replace all previous characteristics and requirements for these substances. Electronic or electrochemical, in certain respects stereochemical corpuscular attributes, are to take the place of all purely material ones. Are substances like hydrogen chloride or sulphur dioxide by their inherent nature, acids? We are reminded of Hittorf who called acids and bases "salts" and then said that "all salts are electrolytes."

A further step towards the generalization of concepts is presented by Germann in an article entitled "A General

[1] The "lone electron pair" or "free electron pair" is the term applied to that pair of electrons required to complete the octette; all incomplete octettes strive to obtain their normal quota of eight electrons. Consequently there is a tendency towards addition reactions as illustrated in the case of ammonia and boron alkyls



Theory of Solvent Systems (Solvo-acids, -bases and -salts)."[1] A general theory of acids, bases and salts is developed in which the solvent is regarded as the parent substance.

"A *parent solvent* is the substance from which a system of solvo-acids, solvo-bases and solvo-salts is derived."

"A *solvo-acid* is any electrolyte, which, in a given solvent, yields cations identical with the cations of the parent solvent, and anions containing, in addition to the atom characteristic of the individual solvo acid, atoms characteristic of the anion of the parent solvent." Thus, Al_2Cl_6 dissolved in phosgene as "parent solvent" yields phosgeno-aluminic acid, $COAl_2Cl_8$. Similar considerations apply when SO_2Cl_2 or $SeOCl_2$ are employed as solvents.

"A *solvo-base* is any electrolyte which, in a given parent solvent, yields simple metal cations, and anions identical with the anions of the parent solvent." As examples may be cited NaCl in liquid hydrogen chloride, KF in HF, KCN in HCN, $Cu(OH)_2$ in H_2O, and PbNH or $NaNH_2$ in liquid NH_3.

"A *solvo-salt* is the electrolyte produced when a solvo-acid reacts with a metal, or with a solvo-base derived from the same or other parent solvent."

The primary assumption in these statements is again the "auto-ionization" of solvents, as

Phosgene, $COCl_2 \rightleftarrows CO^{++} + 2Cl^- = COCl^+ + Cl^-$
Sulfuryl chloride, $SO_2Cl_2 \rightleftarrows SO_2Cl^+ + Cl^- \rightleftarrows SO_2^{++} + 2Cl^-$

SUMMARY

What are really "acids" and "bases"? For many centuries the preparative, synthetic, and analytical chemist has sought to find easily recognizable and experimentally verifiable properties of these classes of substances. He has striven to work out reactions which, on the basis of chemical constitution and characteristic behavior, might serve as clear and definite means of recognizing and identifying such compounds. In time he arrived at the point where he came to regard the individual *material* compon-

[1] J. Am. Chem. Soc., 47, 2461 (1925).

ents, certain atoms in the whole molecule (that is, oxygen or hydrogen) as the determinant factors. Later he found them to be characterized by certain kinetic requirements, such as the easy replaceability of the hydrogen atom of acids by metals, and of bases by acid radicals. Are we not today too eager to classify and arrange schematically our data and to theorize thereon? The modern adept in chemistry is in almost the same quandary as the student in Goethe's "Faust", to whom Mephistopheles says—

> "In short time you will improve, my friend,
> When of scholastic forms you learn the use
> And how by method all things to reduce."

Sad at heart the student replies,

> "So doth all this my brain confound,
> As if a mill-wheel there were turning round."[1]

It would seem that altogether too much emphasis has been placed on "classification." Previously the terms "acid, base, salt," were regarded as practically equivalent, and as constituting a class of chemically active substances, electrolytes, which Hittorf regarded as salts. That belief developed during the middle part of the 19th century when the great advances in organic and inorganic chemistry were being made. It was then linked with definite ionic types, such as the hydrogen and hydroxyl ions of the substances under investigation. The kind of ions and the degree of dissociation of a dissolved electrolyte itself were the objects of examination and the results of the classical theory of dissociation evolved later on in the same century. To-day the emphasis has been shifted to the *solvent*, and the latter's auto-ionization is now regarded as most important.

However, our present knowledge is entangled in altogether too many postulates and assumptions. Take, for instance, an "acid." One group believes the term "acid" to imply something purely relative; another believes it to be fundamentally and quantitatively linked with the

[1] Goethe's *Faust*, English translation by Anna Swanwick (Bell and Sons, London, 1881.)

hydrogen ion. Still other scientists would divide acids into "true and pseudo-acids." Some would even differentiate between "stable" and "unstable" pseudo-acids. Even the typical binary "salts," MX, would now be termed bases!

Berzelius once gave his friend Liebig the following advice:—"We must aim to make scientific theories as clear as possible, but at the same time to change them as little as possible." If we are to call potassium chloride a base or an acid in liquid hydrogen chloride, we should inquire whether any new chemical relationships can be deduced as the result of such a terminology. As far back as 1834, when Faraday created his new electrochemical terms, he said "Names and science are two different things."

The present condition of our concepts, especially in the case of acids, recalls the dispute which was rampant about two centuries ago over the iatrochemical term "sulphur." The theories of that time assigned to "sulphur" a fundamental rôle in the constitution and qualities of substances. One group spoke of "sulphur fixum" in metals; others of a "combustible" kind or principle; a third group of "phlegmatic" sulphur (the principle of sluggishness), while still others insisted that it was identical with "sal acidum." Kunckel, who was an old and experienced chemist, lamented the fact that he "had not yet been able to ascertain what 'sulphur fixum' or the 'sulphur in metals' was. . . . Yes, the word; it has diverted many from the right path. Anything which is to be called sulphur should possess the properties thereof." "You say it makes no difference whether I call it this or that; certainly every one has the right to name his own child, as he wishes; if I were to call an ass an ox, no one would offer opposition thereto, but no man would allow himself to be convinced that an ass were therefore an ox."[1]

Truly, one cannot deny the sagacity and the interesting mental processes which permit us to call potassium chloride or sodium chloride 'bases', when these typical salts are

[1] J. Kunckel von Löwenstern, *Laboratorium Chymicum*, p. 151 et al. (2d ed., Hamburg, 1722).

dissolved in hydrogen chloride; one is also at liberty to call aluminum chloride an acid, when the latter is dissolved in phosgene and eventually forms a complex compound. But on the other hand, one may justly inquire whether there is any practical necessity for such a course of action, whether it represents an advance when scientific names, established as the result of experiment and based on definite theoretical considerations, are taken as marks of distinction for phenomena which differ although they are formally similar. Is there any advantage in such a procedure? Does it not portend a degeneration of our scientific concepts and terms? Would it not be better, in place of the more or less sweeping generalizations, to retain the old established names and concepts with their hydrogen and hydroxyl ions based upon the behavior of aqueous or water-like electrolytic solutions, and to introduce *special* terms for the exceptional cases dealing with new types of solvents? Let us not forget the application of the old classical definitions to analytical, technical, physiological chemistry and biochemical science. It is a remarkable fact, that Wilh. Ostwald in his text-book "The Fundamental Principles of Chemistry"[1] considers neither acids nor bases as such, but discusses only *one* general class, "the salts,"[2] giving for this central concept the following definition: "A salt is a substance whose solutions act as conductors of electricity of the second class." It is evident that this is a transposition of the old sentence of Hittorf: "Electrolytes are Salts."

[1] Translated by H. W. Morse, p. 331 (1917).

[2] The contrast between the classical and the modern epochs is illustrated by the fact that the term "salt" is not mentioned in the subject index of Lewis' book *Valence and the Structure of Atoms and Molecules*.

PART III

ELECTRICAL CONDUCTIVITY OF NON-AQUEOUS SOLUTIONS

CHAPTER VII

"Strong" and "Weak" Electrolytes from the Standpoint of Aqueous Solutions

What is a strong electrolyte?

The concepts "strong" acids, bases or salts, as opposed to "weak" compounds of the same nature, are a heritage from a previous epoch in the development of our theoretical views. They go back to the time when the classical dissociation theory of Arrhenius first appeared, and they form a mental stimulus for modern hypothetical considerations. The infusion and dissemination of electrochemical ideas, and the true evaluation of the Hittorfian thesis that "all electrolytes are salts," led logically and necessarily to the differentiation of "weak and strong electrolytes." These terms and ideas became scientific generalities. They were considered as established and sufficiently explained. The old chemists were entirely justified in this supposition inasmuch as the conditions of experimentation underwent no profound change. The number of investigated electrolytes was limited and, furthermore, they had been studied only in aqueous solution and at ordinary temperatures.

The term "degree of dissociation" ("activity coefficient" α) where $\alpha = \frac{\lambda_v}{\lambda_\infty}$, was first introduced in that memorable treatise of Svante Arrhenius "Concerning the dissociation of substances dissolved in water."[1] In this paper a new and important meaning was given to the conductivity of aqueous solutions, as well as to the numerical value of the equivalent conductivity, λ, at the dilution, v. The greater the value, λ_v, of a solute, the nearer does it approach the maximal value λ_∞ and the condition of complete dissocia-

[1] Z. physik. Chem., **1**, 631 (1887).

tion, where $\alpha \leqq 1$. "Strong" electrolytes are, accordingly, those which conduct the current best. On the basis of his measurements Arrhenius included the following substances among the "strong" bases and acids: $Ba(OH)_2$, $Sr(OH)_2$, $Ca(OH)_2$, LiOH, NaOH, KOH, TlOH, HCl, HBr, HI, HNO_3, $HClO_3$ and $HClO_4$. These, as well as their compounds—salts of strong acids and strong bases—are the best conductors, and may be considered "as being almost entirely split up into their ions." Most of the properties of dilute solutions of this class of compounds are of an additive nature.

Those substances "which are far from completely dissociated even in dilute solution" form a separate group. These include, for instance, "(1) the salts, $HgCl_2$ (and other mercury salts), CdI_2, $CdSO_4$, $FeSO_4$, $MgSO_4$, $ZnSO_4$, $CuSO_4$, and $Cu(CH_3COO)_2$; (2) weak bases and acids such as ammonia and the amines, H_3PO_4, H_2S, $B(OH)_3$, HCN, HCOOH, CH_3COOH, C_3H_7COOH, tartaric, malic and lactic acids. The properties of these will not be of the same additive nature as those first mentioned."

The difference between "strong" and "weak" electrolytes became especially apparent when W. Ostwald set up his general "dilution law" $K = \frac{\alpha^2}{(1 - \alpha)v}$ and applied it to the determination of the constitution and the affinity of acids.[1] "If the theory of electrolytic dissociation is tenable, this formula must express completely the electrical conductivity of binary electrolytes." However, experiment showed that the best conductors and the most highly dissociated substances, that is, the "strong" acids, bases and salts, did not obey the dilution law. That group of substances whose behavior most of all supported the theory of dissociation, was the most contrary when application of the law of mass action to ions was attempted.

This undeniable contradiction has been the subject of much discussion and has been treated both experimentally

[1] Z. physik. Chem., **3**, 170 (1889); **2**, 36, 270 (1888).

and theoretically. Numerous other empirical formulas,[1] designed to embrace the conduct of salts, strong acids and bases, have been proposed in place of Ostwald's dilution law.

Since it was obvious that "strongly dissociated substances" and "strong metallic salts"—salts of the alkali and alkaline earth metals with halide, thiocyanate, and nitrate ions, MeX and MeX_2—required other laws, Kohlrausch[2] proposed the so-called "square root formula"

$$\lambda_0 - \lambda = (\lambda_\infty - \lambda_v) = a \cdot c^{1/2}$$

to express the conductivities of these substances at varying concentrations, c. According to Kohlrausch this expression is satisfactory for salts composed of univalent ions between dilutions where $v \leqq 500$ to $v \geqq 10000$. He says, "it is true that this equation is not derivable from the theory of dissociation, as might be desired. Application of the latter leads to altogether different relationships; however, this fact can hardly be raised as an objection, for it has long since been demonstrated that the theory of dissociation is applicable only to weak electrolytes. The conductivity of strong electrolytes is very evidently dependent upon other processes which take place in solution, among which polymerization is probably of first importance."[3]

Modern definitions.

Arrhenius,[4] the creator of the theory of electrolytic dissociation, divides all electrolytes into two large groups: "the strongly dissociated and the weakly dissociated, or briefly, strong and weak electrolytes. Included in the first group are all salts with very few exceptions . . .; and, in addition, the inorganic univalent and polyvalent acids and bases" (such as HCl, HNO_3, HBr, HI, $HClO_3$, and the bases KOH, NaOH, LiOH, TlOH, and the socalled ammonium bases). "The weak electrolytes include principally

[1] Rudolphi, 1895; van't Hoff, 1895; Kohlrausch, 1895.
[2] Ber., 1215 (1904); Z. Elektrochem., 13, 333 (1907).
[3] *Ibid.*, p. 339 (1907).
[4] *Lehrbuch der Elektrochemie* (1st. ed. 1901; 3d imp. 1915).

the organic acids and bases" (as examples of which may be cited acetic acid and ammonia). "These substances are dissociated only to a slight extent at moderate dilution. Of course compounds are also known which fall in between these two classes, despite the fact that their number is small."

In his widely known textbook,[1] W. Ostwald uses and defines the terms *strong* electrolytes and *weak* electrolytes. "The most strongly dissociated salts are the neutral salts." In the case of acids and bases, the degree of dissociation corresponds to what has been called, rather indefinitely, *strength*, since the strongest acids and bases are those which are most completely ionized."

"*Strong* acids, whose dissociation is of the same order as that of neutral salts, include the halogen hydracids (with exception of hydrofluoric acid), also nitric, chloric, perchloric, sulphuric and the polythionic acids."

Phosphoric, sulphurous, and acetic acids, whose dissociation under ordinary conditions does not exceed ten per cent, are "*moderately strong acids*."

"*Weak acids*, whose percentage dissociation is less than one, include hydrogen sulphide, and carbonic, hydrocyanic, silicic and boric acids. In the case of the latter ones, the degree of dissociation is barely measurable.

"*Strong bases* include the hydroxides of the alkali and alkaline-earth metals, thallium, and the organic quaternary ammonium bases. All these substances are dissociated to nearly as great an extent as the neutral salts.

"The *moderately strong bases* are ammonia and the amine bases of the aliphatic series, as well as silver oxide and magnesia.

"*Weak bases* are the hydroxides of the di- and trivalent metals (with the exception of those mentioned above), the amine bases of the aromatic series . . . as well as the majority of the alkaloids."

Several facts of fundamental importance can be gleaned from this classification. First, the division into "strong"

[1] *Die wissenschaftlichen Grundlagen der analytischen Chemie*. p. 52 (2d ed. 1897); p. 62 (6th ed. 1917).

and "weak" electrolytes includes only the extreme cases. Transitional substances are known which lie between both of these limiting groups. Second, accurate numerical data of α (degree of dissociation) for these limiting cases have been omitted. The minimum values for "strong electrolytes," as well as the maximum values of α for "weak" ones can be said to possess only a conventional character. Third, for the purposes of orientation it may be assumed that the typical binary neutral salts of mineral acids and alkalies, as well as the acids and alkalies themselves, make up the class of "strong" electrolytes. Thus, the historical salts and salt formers again arise in our modern conceptions.

Similarly compounded salts are dissociated to the same extent.

A comparison of the various "strong" electrolyte-salts with reference to a possible connection between chemical composition and the corresponding degree of dissociation $\alpha = \lambda_v/\lambda_\infty$ led to new facts. In his classic textbook[1] Nernst says that "the change in conductivity of all salts composed of univalent radicals, at concentrations from c = 0.1 downwards, is almost identical; that is, *they are dissociated to almost the same degree in equivalent solutions.*" . . . Salts of the alkalies, ammonium, thallium and silver with monobasic acids are dissociated in dilute solutions at equivalent concentrations to the same degree and to quite a great extent." Even electrolytes which break up into more than two ions are included, for, he says, "*similarly compounded salts are dissociated to the same extent in equivalent solutions.*"

Let us determine whether these conclusions can be substantiated by reliable conductivity data. For this purpose we will choose a number of typical binary as well as ternary salts, containing a divalent cation and univalent anion. Let the temperature be varied from 0° to 100°, in order to determine the influence of this factor. The dilution v (liter of water) where v = 10 to 10000 lit., is taken as the third variable.

[1] *Theoretische Chemie*, p. 389, 540 (7th ed. 1913); p. 417, 581 (8th ed. 1921).

TABLE II

Binary Salts

$t = 18°$; $\alpha_v = \lambda_v/\lambda_\infty$;[1] Product of ionic valences, $n_1 \cdot n_2 = 1$

Salts	v = 10	20	50	100	200	500	1000	2000	5000	10 000
KCl	0.8624	0.8911	0.9235	0.9425	0.9578	0.9723	0.9803	0.9863	0.9913	0.9936
NaCl	0.8453	0.8792	0.9152	0.9365	0.9532	0.9696	0.9781	0.9845	0.9904	0.9931
LiCl	0.8335	0.8709	0.9093	0.9318	0.9497	0.9670	0.9761	0.9829	0.9895	0.9924
KNO_3	0.8293	0.8694	0.9116	0.9352	0.9532	0.9701	0.9784	0.9847	0.9905	0.9931
$NaNO_3$	0.8296	0.8684	0.9085	0.9322	0.9504	0.9676	0.9768	0.9833	0.9895	0.9930
Mean value found α_m =	0.839	0.875 (0.8719)	0.9136 (0.9111)[2]	0.9356	0.9529	0.9693	0.9780	0.9843	0.9902	0.9930
Calc. $\alpha_v = \frac{v^{1/2}}{v^{1/2}+0.692}$	0.821	0.8660	0.9109	0.9353	0.9533	0.9699	0.9785	0.9843	0.9903	0.9931
Calc. by Ghosh[1] α =	0.8410	0.8719	0.9041	0.9230	0.9384	0.9542	0.9634	0.9712	0.9784	0.9829
Mean value according to Noyes[3] α =	0.833	0.874	—	0.934	0.953	0.969	0.978	—	—	—

[1] Arrhenius, Z. physik. Chemie, **100**, 16 (1922).
[2] The data in curves have been calculated without KCl.
[3] A. A. Noyes and K. G. Falk, J. Am. Chem. Soc., **34**, 476 (1912), at 18°.

Table III

Ternary Salts

$t = 18°$; $\alpha_v = \lambda_v/\lambda_\infty$; $n_1 \cdot n_2 = 2$.

Salts	v = 20	50	100	200	500	1000	2000	5000	10 000
½ $MgCl_2$	0.795	0.847	0.881	0.909	0.938	0.954	0.967	0.978	0.982
½ K_2SO_4	0.766	0.830	0.870	0.904	0.940	0.953	0.966	0.978	0.983
½ $CaCl_2$	0.791	—	0.879	—	0.939	0.955	—	0.977	0.984
½ $RaBr_2$	0.791	0.842	0.876	0.903	0.932	0.951	0.963	0.977	0.985
½ $Ba(NO_3)_2$ (Noyes)	0.743	—	0.864	—	0.938	—	—	—	—
Mean value calc.	0.777	0.840	0.874	0.905	0.937	0.953	0.965	0.9775	0.984
$\alpha = \frac{v^{½}}{v^{½} + 2 \times 0.692}$	0.764	0.836	0.878	0.911	0.942	0.958	0.970	0.9808	0.986
Calc. by Ghosh	0.729	0.792	0.831	0.863	0.898	0.918	0.935	0.951	0.962
Calc. by Noyes and Falk (1912) for MCl_2	0.801	0.850	0.883	0.910	0.939	0.955	0.967	0.978	0.984

TABLE IV
Binary Salts
$t = 25°$; $\alpha_v = \lambda_v/\lambda_\infty$; $n_1 \cdot n_2 = 1$

Salts	v = 32	64	128	256	512	1024	2048
KCl (R. Lorenz)	0.902	0.9257	0.9445	0.9591	0.9700	0.9788	0.9857
NaCl "	0.895	0.9203	0.9411	0.9567	0.9693	0.9785	0.9852
$KMnO_4$ "	0.894	0.9218	0.9421	0.9579	0.9700	0.9792	0.9857
NaBr "	0.898	0.9275	0.9452	0.9604	0.9714	0.9796	0.9860
KBr "	0.904	0.9236	0.9428	0.9591	0.9700	0.9790	0.9858
CH_3COONa "	0.886	—	—	0.9560	—	0.9800	—
LiCl (0°)	0.895		0.945			0.980	(Washburn)
RbCl (25°)	0.898		0.946			0.982	(Bredig)
NH_4Cl (25°)	0.898		0.945			0.981	(Bredig)
Calc. (Walden)	0.893	0.920	0.9423	0.9585	0.9703	0.9788	0.9851

Table V

Ternary Salts

$t = 0°$ and $25°$; $n_1 \cdot n_2 = 2$

Salts	v = 32	128	512	1024	
$\frac{1}{2}\,BaCl_2$ (25°)	α = 0.818	0.888	0.943	0.961	(Ley)
$\frac{1}{2}\,Ba(ClO_4)_2$ (25°)	α = 0.825	0.890	0.943	0.967	(Ley)
$\frac{1}{2}\,Sr(NO_3)_2$ (0°)	α = —	0.884	0.939	0.961	(Kahlenberg)
$\frac{1}{2}\,[Pt(NH_3)_4]Cl_2$ (25°)	α = 0.804	0.887	0.934	0.960	(R. Lorenz)
$\frac{1}{2}\begin{bmatrix} CH_2NH_3 \\ \vert \\ CH_2NH_3 \end{bmatrix}Cl_2$ (25°)	α = 0.812	0.892	0.943	0.950	(Bredig)
$\frac{1}{2}\,[(CH_2)_4(NH_2 \cdot H)_2]Cl_2$ (25°)	α = 0.802	0.881	0.937	0.958	(Bredig)
Average value		0.887	0.940	0.959	
Calc. (Walden)	α = 0.803	0.891	0.942	0.959	

TABLE VI

Degree of Dissociation $\alpha_v = \lambda_v/\lambda_\infty$ *at various temperatures.**

	v = 100	200	500	1000	2000	5000	λ_∞
			$t = 0°$				
KCl	0.943	0.956	0.971	0.978	0.984	—	82.1
$KClO_4$	0.936	0.954	0.971	0.978	0.984	—	77.68
KNO_3	0.938	0.957	0.971	0.979	0.986	—	80.7
Potassium picrate	0.935	0.953	0.971	0.980	0.986	0.991	55.5
Average value	0.938	0.955	0.971	0.979	0.985		
			$t = 18°$				
KCl	0.942(?)	0.957	0.972	0.980	0.985	0.991	130.0
$KClO_4$	0.932	0.952	0.969	0.979	0.986	—	122.5
KNO_3	0.936	0.954	0.970	0.979	0.985	0.991	126.35
Potassium picrate	0.931	0.950	0.968	0.977	0.984	0.991	89.6
Average value	0.933	0.953	0.970	0.979	0.985	0.991	
Calculated	0.935	0.954	0.970	0.9785	0.9843	0.9903	
			$t = 100°$				
KCl	0.925	0.946	0.964	0.974	0.982	0.989	407.5
$KClO_4$	0.929	0.950	0.968	0.978	0.985	0.993	406.0
KNO_3	0.924	0.946	0.964	0.976	0.983	0.989	376
Potassium picrate	0.923	0.947	0.965	0.975	0.983	0.990	385
	0.922	0.943	0.966	0.976	—	—	289.5
Average value	0.924	0.946	0.965	0.976	0.983	0.991(990)	

* Walden and Ulich, Z. physik. Chem., 106, 49 (1923).

The calculated values for percentage dissociation are based on the assumption that all "strong" salts of the same type (in which, however, binary and ternary salts are distinct classes) are ionized similarly and to an equal degree.[1] In Table VII are given the values for degree of dissociation calculated from the formula:

$$\alpha_{calc.} = \frac{1}{1 + \frac{n_1 . n_2 \times 0.692}{v^{1/2}}}$$

It is evident from the values given in Tables II to VI for various typical inorganic binary and ternary salts at temperatures between 0° and 100°, that Nernst's views are correct. Similarly constituted salts are actually found to be dis-

[1] P. Walden, Z. physik. Chem., 108, 341 (1924).

sociated to a like degree throughout a wide dilution range (where v = 100 to 10 000 liters). Average values which may be regarded as characteristic are accordingly obtained for every dilution and every class of compounds. These average

Table VII

$n_1 \cdot n_2$	v = 10	20	100	200	500	1000	10 000
1	$\alpha_1 = 0.821$	0.866	0.935	0.954	0.970	0.9785	0.9931
2	$\alpha_2 = 0.696$	0.764	0.878	0.911	0.942	0.958	0.986
3	$\alpha_3 = 0.604$	0.683	0.828	0.872	0.915	0.938	0.979
4	$\alpha_4 = 0.533$	0.617	0.783	0.836	0.889	0.9198	0.973

values can, furthermore, be computed with sufficient accuracy by application of the empirical equation

$$\alpha_{calc.} = \frac{v^{1/2}}{v^{1/2} + n_1 \cdot n_2 \times 0.692}$$

where n_1 and n_2 represent, respectively, the valencies of the anion and the cation.

Hydrochlorides of the Alkylated Ammonium Bases in Water at t = 25°

Let us next investigate another class of binary salts, namely, the chlorides of the alkylated ammonium bases. As uni-univalent salts they correspond in type to the inorganic normal salt, potassium chloride. They are stable in aqueous solution at 25°C. They admit great variation in the constitution of the cations (methyl, ethyl, etc., mono-, di-, tri-, tetra-alkylated). They are of particular interest because of their solubility in non-aqueous solvents. Because of their unique adaptability to study in these media they will be discussed in this connection later on.

Ten salts may be chosen from among the numerous measurements of Bredig[1] to determine the influence of the degree of alkylation, (mono-, di-, tri-, and tetra-substituted ammonium salts), and of the size of the substituted alkyl upon the degree of dissociation.

In Table VIII are given the values for the degree of dissociation $\alpha = \mu_v/\mu_\infty$ at dilutions where v = 32, 128, 512, and 1024, as calculated from Bredig's data for the equivalent

[1] Z. physik. Chem., **13**, 208 (1894).

conductivity of these substances in aqueous solution at 25° at dilutions ranging from 32 to 1024 liters. The maximum value μ_∞ is here determined in every case by extrapolation, but by a different method than that used for λ_∞ in the previous tables.

TABLE VIII

Influence of Alkylation Upon Percentage Dissociation (α) of Substituted Ammonium Salts

	Salts	v = 32	128	512	1024
I.	Mono-alkylated bases:				
	Ethylamine hydrochloride $(C_2H_5)NH_2 \cdot HCl$	0.879	0.933	0.965	0.997
	Propylamine hydrochloride $(C_3H_7)NH_3Cl$	0.872	0.930	0.962	0.975
	Isoamylamine hydrochloride $C_5H_{11}NH_3Cl$	0.868	0.927		0.973
II.	Di-alkylated bases:				
	Di-ethylamine hydrochloride $(C_2H_5)_2NH_2Cl$	0.866	0.928	0.963	0.976
	Dipropylamine hydrochloride $(C_3H_7)_2NH_2Cl$	0.856	0.923		0.972
	Di-isoamylamine hydrochloride $(C_5H_{11})_2NH_2Cl$	0.850	0.921	0.957	0.970
III.	Tri-alkylated bases:				
	Tri-ethylamine hydrochloride $(C_2H_5)_3NHCl$	0.859	0.926	0.962	0.975
	Tripropylamine hydrochloride $(C_3H_7)_3NHCl$	0.848	0.923		0.971
	Methyl di-ethylamine hydrochloride $(CH_3)(C_2H_5)_2NHCl$	0.865	0.927		0.974
IV.	Tetra-alkylated bases:				
	Tetramethylammonium chloride $N(CH_3)_4Cl$	0.871	0.932	0.966	0.979
	Tetra-ethylammonium chloride $N(C_2H_5)_4Cl$	0.861	0.926	0.959	0.972
	Amyl tri-ethylammonium chloride $N(C_2H_5)_3(C_5H_{11})Cl$	0.852	0.919		0.971
	Average values	0.862	0.926	0.963	0.974
	(Comp. Table IV, calculated:	0.893	0.942	0.970	0.9788)

These figures show (1) that the chlorides of the alkylated ammonium bases, not only the primary, secondary and tertiary, but also the quaternary compounds, possess

practically the same degree of dissociation, $\alpha = \mu_v/\mu_\infty$, in equivalent solutions where v = 32 to 1024 liters. As binary uni-univalent salts of the same type, they are found to possess the same electrolytic behavior. Neither the number, nor the size, nor the nature of the alkyl groups in the ammonium radical has any noticeable effect upon the numerical values of the degree of dissociation. (2) A comparison of the α-values of this class of salts with those tabulated previously for strong inorganic salts reveals a slight retardation in the case of the alkylated ammonium salts at dilutions between v = 32 to 512. However, this difference disappears at higher dilutions, and where v = 1024 the α-values are found to be practically identical with those of the typical binary salts.[1]

The similarity of the mono-, di-, tri-, and tetra-alkylated ammonium chlorides with one another is brought out still more sharply by a comparison of the values of the dissociation constants, as calculated by means of Rudolphi's equation

$$K = \frac{\alpha^2}{(1 - \alpha)\sqrt{v}}$$

Data are given in Table IX to illustrate this point.

Table IX

Dissociation Constants of Various Alkylated Ammonium Chlorides

Salts		$K = \frac{\alpha^2}{(1-\alpha)\sqrt{v}}$
Mono:	$N(C_5H_{11})H_3Cl$	1.02
	$N(C_2H_5)H_3Cl$	1.28
Di:	$N(C_2H_5)_2H_2Cl$	1.01
	$N(CH_3)_2H_2Cl$	1.18
Tri:	$N(C_2H_5)_3HCl$	1.01
Tetra:	$N(C_2H_5)_4Cl$	1.01
	$LiCl$	0.98
	$AgNO_3$	1.11

The numerical values of K are all of the same order: mono-, di-, tri- and tetra-ethylated salts have an identical constant K.

[1] It is entirely possible that this retardation in α values is due to the fact that the limiting conductivity, μ_∞, was calculated by a different method, one known to give high results.

Strong Electrolytes possess a High Degree of Dissociation.

$$\alpha = \frac{\lambda_v}{\lambda_\infty}.$$

If we wish to test this statement regarding the degree of dissociation of "strong" electrolytes for its general applicability to all kinds of solvents, difficulties of fundamental importance arise which must first be cleared up before any further work is done. If the equivalent conductivity, λ_v, be considered a physical constant, since it is obtainable by direct measurement, it is evident that the new definition presupposes the inclusion of the limiting value, λ_∞, as another constant characteristic of the electrolytic nature of a substance. This brings up a new problem, namely, the *evaluation of the conductivity* λ_∞ *at infinite dilution* ($v = \infty$) with utmost accuracy. Naturally, an experimental determination of this figure can only lead to values which approach it. At best, results at finite dilutions may be obtained which permit extrapolation to infinite dilution, provided that the change in the conductivity, λ_v, at decreasing concentrations is so regular that that part of the curve which can no longer be determined experimentally is an unquestionable continuation of that portion which was so obtained. It is also necessary that the measured λ_v values be as accurate as possible and be determined up to the highest feasible dilutions.

Earlier investigations by Kohlrausch demonstrate that in the case of water and of aqueous salt solutions, the limiting value is not reached even where $v = 10000$ mol/liters. Using "ultra-pure" water, Weiland (1918) increased the dilutions to 50000 and 100000 liters. From these measurements Washburn[1] concludes that at 18° and $v = 10000$, the conductivity values for strong binary salts are still 0.475% off from the limit λ_∞, or that $\lambda_\infty = 1.00475 \times \lambda_{10000}$. The investigations of Bencowitz and Renshaw[2] also show that the salts of the ammonium bases do not reach the limiting value even at dilutions $v = 16000$ liters.

[1] J. Am. Chem. Soc., 40, 150 (1918).
[2] *Ibid.*, 48, 2146 (1926).

These facts are of importance when we turn from aqueous to non-aqueous solutions, and when we wish to pass judgment with reference to the dilutions at which similar conditions are attainable in these much less powerful ionizing media. It is clear at the start that the maximal value in such cases is obtainable only where the dilution is well above 50000—depending upon the dielectric constant of the solvent. The non-observance of these relationships, together with faulty experimental technique, and the use of impure materials, has caused many deserving investigators in the electrochemistry of non-aqueous solvents, to claim that they had attained this limiting value at finite dilutions. This condition is supposed to have been reached for potassium iodide in methyl alcohol at dilutions $v = 2000$–4000 (Jones and Kreider, 1911); in ethyl alcohol, $v = 3200$–8000–10000 (the same); for sodium iodide in acetone with $v = 1024$, and potassium iodide in the same solvent with $v = 2048$ (Carrara 1897). Dutoit[1] tried to reach these limiting values experimentally by studying extremely dilute solutions.

No experimental method for the direct determination of limiting conductivities, λ_∞ (or λ_0) has yet been found. These constants have been obtainable only by extrapolation from the λ values of more concentrated solutions to the λ_∞ value at zero concentration. In 1885 Kohlrausch worked out the following functional relationship between the equivalent conductivity λ_v and the concentration c ($= 1/v$) for dilute aqueous solutions:

$$\lambda_\infty - \lambda_v = Kc^{1/3} = \frac{K}{v^{1/3}},$$

or

$$(\lambda_\infty - \lambda_v)\sqrt[3]{v} = K$$

Using this formula the curves obtained for univalent salts in water even up to $v = 1$ (normal solutions) were often linear (Kohlrausch). Since 1903 Walden[2] has used this "cube-root formula" almost exclusively in his researches.

[1] Z. Elektrochem., **12**, 643 (1906).
[2] Walden, Z. physik. Chem., **54**, 129, 230 (1905).

The highest dilutions employed were 8000–10000 mol/liter, and based on the degree of dissociation $\alpha = \lambda_v/\lambda_\infty$ the results for these dilutions of non-aqueous solutions approximated those required by aqueous solutions at dilutions v = 10 to 100. Therefore, it may be supposed that both aqueous and non-aqueous solutions are in a correspondent state. The same equation has also been used by Philip and Courtman[1] and particularly by H. Goldschmidt[2] (in Oslo) since 1916.

Even if the Kohlrausch formula is an empirical rule, the Ostwald dilution law

$$K = \frac{\lambda_v^2}{v\,(\lambda_\infty - \lambda_v)\lambda_\infty} = \frac{\alpha^2}{(1 - \alpha)v}$$

affords a method, based theoretically upon the mass law, for the determination of the conductivity at infinite dilution. It is applicable in all cases where the law is valid for the given electrolyte and solvent under investigation.

In this manner Dutoit and Gyr (1909) determined the limiting values in sulphur dioxide solutions. Kraus and Bray[3] have very cleverly extended the Ostwald equation and given it the form

$$\frac{(c\alpha)^2}{c(1 - \alpha)} = K + D\,(c\alpha)^m$$

in which D and m are empirical constants. It may be mentioned in this connection that in sufficiently dilute solutions, where c is very small, the last member in the above expression may be neglected. Kraus and Bray applied this equation to the available data known at that time.[4] The limiting values, λ_∞, and the dissociation constant K have been determined repeatedly by application of the law of mass action: thus for NaI in propyl and isoamyl alcohols

[1] J. Am. Chem. Soc., **97**, 1261 (1910).
[2] Z. Elektrochem., **22**, 340 (1916); Z. physik. Chem., **99**, 161 (1921).
[3] J. Am. Chem. Soc., **35**, 1315 (1913).
[4] The limiting values determined in this way are invariably low; thus KCl in water at 18° has a λ_∞ of 128.3 (instead of 129.98–130.1); for KI in sulphur dioxide at −10°, λ_∞ = 199, whereas extrapolation from Franklin's data using the square-root formula gives λ_∞ = 240–245; for KI in pyridine at 20°, the value 62.1 is obtained, for NaI, 59.9, whereas the $\sqrt{c}$ formula gives λ_∞ = 71.3 and 66.4, respectively, etc.

by Keyes and Winninghoff;[1] in isoamyl alcohol[2] by Kraus and Bishop;[3] in phenol solutions by Kraus and Kurtz;[4] in formic acid by Schlesinger and his co-workers;[5] for KI in nitromethane by Philip and Oakley.[6]

Assuming the general validity of the Ostwald equation and giving it the form

$$\lambda_\infty = \lambda_c (1 + \lambda_c c/\lambda_\infty K),$$

the conductivity at infinite dilution, λ_∞, may be obtained with sufficient accuracy at high dilutions (or when c is small and $\lambda_c/\lambda_\infty \sim 1$) from the expression

$$\lambda_\infty = \lambda_c (1 + c/K)$$

provided K is known for a definite λ_c value.[7]

Square-Root Formula of Kohlrausch: $\lambda_\infty - \lambda_v = a \cdot c^{1/2}$

In the year 1900 Kohlrausch applied the formula $\lambda_\infty - \lambda_v = a\sqrt{c}$ to aqueous salt solutions at "great dilutions," and found it to fit best in cases v = 500 to 10000.

Walden[8] was the first to undertake an extensive proof of the Kohlrausch equation, as well as the Lorenz equation

$$\lambda_\infty - \lambda_v = bc^{0.45}$$

for *non-aqueous* salt solutions. By extending the empirical relationship of Ostwald-Walden-Bredig (the O.-W.-Br. rule) the following form may be given to the square-root formula

$$\lambda_\infty - \lambda_v = dv = \left(\frac{K}{\epsilon\eta}\right)\sqrt{c} = \frac{65.7}{\epsilon\eta v^{0.5}} = \frac{65.7}{\epsilon\eta}\sqrt{c}$$

where 65.7 is a universal constant, ϵ and η represent, respectively, the dielectric constant and the viscosity of

[1] J. Am. Chem. Soc., **38**, 1178 (1916).

[2] For NaI the dissociation constant, $K = 2.933 \times 10^{-4}$ and $\lambda_\infty = 11.059$ at 25°, whereas the $\sqrt{c}$ formula gives the value $\lambda_\infty = 11.72$ by extrapolation.

[3] J. Am. Chem. Soc., **44**, 2206 (1922).

[4] J. Am. Chem. Soc., **44**, 2463 (1922).

[5] J. Am. Chem. Soc., **36**, 1589 (1914); **38**; **41**.

[6] J. Chem. Soc., **125**, 1189 (1924).

[7] Washburn, J. Am. Chem. Soc., **40**, 153 (1918); Bencowitz and Renshaw, *ibid.*, **47**, 1915 (1925).

[8] Z. anorg. Chem., **115**, 49, 81 (1921).

the solvent under investigation, and v the dilution in liters per mol. It is noteworthy that a in the Kohlrausch equation is replaced by a universal constant, and two others which represent definite physical constants of each individual solvent. Therefore, $a = K/\epsilon\eta$

Walden[1] was further able to point out the connection between the limiting conductivity and the square root formula by setting up and verifying the following empirical equation, applicable to both aqueous and non-aqueous solutions.

$$\lambda_\infty = \lambda_v \left(1 + \frac{K_1}{v^{0.5}}\right) = \lambda_v (1 + K_1\sqrt{c})$$

or

$$\lambda_\infty - \lambda_v = K_1\lambda_v\sqrt{c}$$

Walden and his co-workers[2] subsequently applied the square-root law to their own conductivity measurements in methyl and ethyl alcohols at dilutions of v = 100 to 10000 and at the temperatures 0°, 25° and 56°, including with these the data obtained by Morgan and Lammert[3] for acetophenone solutions.

Independent investigations by Philip and Oakley[4] with reference to the applicability of both the square-root formula, $c^{0.5}$, and the $c^{0.45}$ formula previously mentioned, were carried out on solutions of potassium iodide in nitromethane, at temperatures varying from 0° to 85°. In both cases they found the λ-values to be *rectilinear* functions of the dilution. The most detailed investigation of uni-univalent salts was made soon thereafter by J. E. Frazer and H. Hartley[5] who found the λ-values to be in close agreement with those required by the square-root formula $\lambda_c = \lambda_\infty - a\sqrt{c}$ at dilutions varying from v = 500 to 10000 liters at 25°.

Another empirical relationship for aqueous solutions which deals with the square root of the concentration c,

[1] Z. physik. Chem., **108**, 341 (1924).
[2] Walden, Ulich and Laun, Z. physik. Chem., **114**, 295 (1924); Walden and Ulich, *ibid.*, **114**, 297 (1924).
[3] J. Am. Chem. Soc., **46**, 1117 (1924).
[4] J. Chem. Soc., **125**, 1189 (1924).
[5] Proc. Roy. Soc. London, **A109**, 351 (1925).

is advanced by C. W. Davies[1] for concentrations less than 0.002 N, where K is a constant:

$$\lambda_\infty - \lambda_c = K\sqrt{c\lambda_\infty}$$

According to Frazer and Hartley[2] this equation does not hold for methyl alcohol solutions.

It may here be noted that the postulations of Debye and Hückel[3] have given a theoretical foundation to the Kohlrausch square-root formula, and have aligned it with the modern theory of dissociation. The experimental investigations cited above have furthermore demonstrated that this law is also valid for non-aqueous salt solutions over wide temperature ranges. Although these observations had been confined primarily to good ionizing solvents such as methyl and ethyl alcohols and nitromethane, Walden, Ulich and Busch[4] have also shown the law to apply in the case of acetone. It was also found to hold for salt solutions in weak ionizing solvents having a dielectric constant $\epsilon \leqq 10$, such as the chlorinated hydrocarbons, ethylene chloride,[5] dichlorethylene and tetrachlorethane ($\epsilon = 8.15$).[6]

Dissociation Constants as Means of Distinction between Strong and Weak Electrolytes.

Van Laar[7] was one of the first to express the opinion that the true degree of dissociation of all strong electrolytes in moderately dilute solution practically may be equal to unity. He gives the following definition[8] for strong and weak electrolytes: "The difference between 'strong' and 'weak' electrolytes is not due to secondary influences of powerful electrostatic fields around the ions, but to the value of the ordinary, thermodynamical dissociation constant K. . . . If the value of K is high, the electrolyte may be called a strong one; if it is small, the electrolyte

[1] J. Phys. Chem., **29**, 473, 973, 977 (1925).
[2] Proc. Roy. Soc. London, **A109**, 367 (1925).
[3] Physik. Zeit., **24**, 320 (1923); Ergebnisse der exakten Naturw., 3, 270 (1924).
[4] Z. physik. Chem., **123**, 455 (1926).
[5] Unpublished investigations by Walden and Busch, 1927.
[6] Unpublished investigations by Walden and Gloy, 1927.
[7] Arch. Teyler, (2) **7**, Part I, p. 1 (1900).
[8] Z. anorg. Chem., **139**, 108 (1921).

is weak. . . . Naturally, Ostwald's dilution law is applicable to both kinds of electrolytes:

$$\frac{(\alpha c)^2}{(1-\alpha)c} = K \times \text{elect. factor}$$

In the case of strong binary electrolytes, where α is always in the neighborhood of 1, even in moderately dilute solutions, an experimental verification of this law can hardly be expected."

There are a number of points in this definition pertinent to the subject under discussion, which should be emphasized. First, the statement that Ostwald's law is valid for all kinds of electrolytes; second, the *size of the dissociation constant*, as obtained by application of this law, is made the deciding factor as to whether an electrolyte may be called strong or weak, although it is left an open question as to where the point of demarcation lies; third, that an experimental determination of K on the basis of the dilution law is practically hopeless. However, it should be remembered that recent experimental work has extended the limits of conductivity measurements. Exact determinations of λ_v-values of solutions have been performed even at dilutions $v = 50000$ to 100000.

Sutherland was the next to assume (in 1907) the complete dissociation of strong electrolytes. Bjerrum has subsequently become the independent champion of this idea, and has developed and verified it experimentally. Remarkable, indeed, is his statement,[1] "With our present knowledge we must regard it as a mistake to consider the conductivity coefficient, μ_v/μ_∞, of a strong electrolyte as meaning the same as the degree of dissociation, and to attempt to apply the law of mass action to it." Further, "Our recent theories have directed attention to the determination of the dissociation constants of practically 100% dissociated electrolytes. I venture to emphasize the fact that we may possibly obtain thereby a measure of the true strength of

[1] Ergebnisse der exakten Naturw., 5, 137ff. (1926).

electrolytes. Interesting results are to be expected here when sulphuric acid and the sulphonic acids are employed."

The important points in this quotation are the rejection of the classical degree of dissociation, μ_v/μ_∞, as a basis for the determination of the dissociation constant in accordance with the dilution law, and furthermore, the prominence given to the possibility and the necessity for the determination of the "dissociation constant" for "totally dissociated" electrolytes on the basis of this new conception.

Besides Bjerrum a number of other investigators, among whom may be mentioned Milner (1912–1913), P. Hertz (1912), Ghosh (1918, 1921), and particularly Debye and Hückel (1923 and later), have been active in working out a general theory for strong electrolytes.

Hückel[1] arrives at his theory of strong electrolytes in the following manner. "Let us assume that there exist completely dissociated electrolytes and let us calculate, theoretically, how these should act. One ascertains that there are electrolytes which behave in accordance with such deduced properties. These will now be assumed to be wholly dissociated. These are the electrolytes which have been designated as 'strong.'" It is evident that this definition has been worded very carefully. No references to the constitution of electrolytes, no dependence upon the type, no general prediction as to their strength are given. It therefore becomes necessary to determine separately for each individual electrolyte whether or not it is to be called a "strong electrolyte."

Let us now see what some of our standard textbooks have to say about "strong electrolytes."

In his "A System of Physical Chemistry,"[2] W. C. McC. Lewis divides all electrolytes into two groups on the basis of the degree of dissociation $\alpha = \lambda_v/\lambda_\infty$.

"A. Strong electrolytes (good conductors of electricity)."[3] Typical examples are NaCl, KCl, HCl, K_2SO_4,

[1] Physik. Zeit., 27, 97 (1925).

[2] Vol. I, p. 276 (1923).

[3] Good conductivity in aqueous solutions is therefore considered a distinctive mark of a strong electrolyte, or the term "good conductor" is synonymous with the term "strong electrolyte," and *vice versa*.

$AgNO_3$. Their degree of dissociation values at 18° follow:

	NaCl	KCl	HCl	$\frac{1}{2}K_2SO_4$	$AgNO_3$	$\frac{1}{2}BaCl_2$	$\frac{1}{2}CuSO_4$
v = 10	0.85	0.86	0.93	0.72	0.81	0.76	0.90
v = 100	0.94	0.94	0.97	0.87	0.93	0.88	0.63

"B. The extent of dissociation in the case of weak electrolytes (those which conduct current badly)." Acetic acid and ammonia are given as illustrations. To afford a means of comparison with A the α_{10} and α_{100} values at 25° are given.

	CH_3COOH	NH_3 (or NH_4OH)
v = 10	0.015	0.014
v = 100	0.044	0.051

The numerical data refer to aqueous solutions and bring out clearly the difference in behavior or dissociation tendency between the two classes of electrolytes.

Lewis also discusses "The Anomaly of Strong Electrolytes." He says: "The most remarkable phenomenon in the equilibria relations of electrolytes in aqueous solution is that all (or nearly all) strong electrolytes—throughout the range of dilution 10 to 1000 liters—do not even approximately obey the dilution law. . . . All the ordinary inorganic salts (with the exception of cadmium and mercuric halides, mercuric cyanide and one or two ferric salts), all the ordinary inorganic acids and bases (with the exception of weak acids, such as H_2S, H_3BO_3, CO_2, HNO_2, SO_2, phosphorous acid, and ammonia) dissociate in such a manner that when one calculates the 'constant' for each dilution, it is found that the resulting numbers scarcely remain even of the same order of magnitude."

In this statement the anomalous behavior of strong electrolytes—good conductors—is especially emphasized. The K values show a march, decreasing more and more as the concentration diminishes, a fact which is noticeable over a dilution range v = 10 to 1000 liters. These phenomena present two problems; first, the change in K values when dilutions are *increased* from v = 1000 to the extreme workable limit; second, if at the highest dilutions *constant*

values for K are really obtained, whether the latter may then be construed as the true dissociation constants of strong electrolytes, despite the fact that they are calculated on the basis of the formula $\alpha = \lambda_v/\lambda_\infty$. A third question might then arise as to whether there is any agreement between these dissociation constants and those determined on the basis of modern theories.

An extension of conductivity measurements for dilutions much over 1000 liters necessitates a refined experimental technique which will produce absolutely accurate results even at the extreme workable limits. It is also necessary to obtain reliable figures for the conductivity μ (or λ) at infinite solutions. Then only can the results for the degree of dissociation $\alpha = \lambda/\lambda_\infty$ be determined with utmost accuracy.

It is chiefly to the credit of American physical chemists, who worked with great precautions using "ultra-pure" water (conductivity $K \leqq 0.06 \times 10^{-6}$) as solvent, that the field of highest dilutions has been studied conductimetrically. Let us consider several series of model measurements of this kind and from the data calculate the Ostwald dissociation constant $K = \frac{\alpha^2}{(1-\alpha)v}$. We choose the three "strong" electrolytes KCl, HIO_3 and HCl.

H. I. Weiland[1] gives the following results for *potassium chloride* at 18°, where the dissociation constant

$$K = \frac{\alpha^2}{(1-\alpha)v} \text{ and } \alpha = \frac{\lambda_v}{\lambda_\infty}:$$

v	λ_v	α	K
1000	127.258	0.9816	0.0524
5000	128.676	0.9925	0.0265
10000	129.029	0.9953	0.0210
20000	129.320	0.9975	0.0201
50000	129.511	0.9990	0.0200
100000	129.573	0.9995	0.0200
∞ [2]	129.64	1.0	0.0200 ± 0.001

[1] J. Am. Chem. Soc., **40**, 756 (1918).
[2] See also Kraus, *ibid.*, **42**, 1, 1087; Washburn, *ibid.*, **42**, 1077, 1090 (1920).

The results obtained by H. C. Parker[1] for *hydrochloric acid* at 25° follow:

v	λ_v	α	K
500	419.867	0.9863	0.1421
1000	421.997	0.9913	0.1131
1666	423.302	0.99439	0.1056
2000	423.683	0.99528	0.1051
5000	424.883	0.99810	0.105
10000	425.286	0.99905	0.105
20000	425.489	0.99953	0.105
∞	425.69	1.0	0.105

The dissociation constant K of hydrogen chloride in water is accordingly $K = 1.0 \times 10^{-1}$. This determination of the dissociation constant, K = 0.105, of hydrogen chloride in water brings up several interesting points. Schreiner[2] has investigated the dissociation of acids in the alcohols. He assumes incomplete ionization and introduces the activity coefficient f (of H^+ and Cl^-) into the law of mass action $\frac{c_i^2 \cdot f^2}{c_{HCl}} = K_0$. He finds the dissociation constants of hydrogen chloride to be

in ethyl alcohol: $K_0 \sim 10^{-2}$
in methyl alcohol: $K_0 \sim 10^{-1}$

Goldschmidt has found as a result of his investigations on the carboxylic acids that there is an average difference of 10^6 between the dissociation constants of these substances in water and in alcohol. On this basis HCl with a K_0 value of 10^{-2} in alcohol should have a dissociation constant of 10^4 in water. This throws an altogether different aspect on the situation, as Parker's constant is only 1/10000 of that which might be expected from Schreiner's figures. It is perfectly obvious that we here confront a condition of affairs which is urgently in need of revision and settlement. It is not conceivable that, in view of the great dilutions employed (v = 20000 to 100000), a correction for interionic forces in this case could effect such an enormous

[1] J. Am. Chem. Soc., **45**, 2027 (1923).
[2] Z. physik. Chem., **111**, 419 (1924).

shift (10^4 to 10^5) in the K values, especially since, as we shall presently see, the old and new K values for moderately strong electrolytes are in fairly close agreement.

Corresponding data[1] for the *iodic acid*, HIO_3, at 25° are also given:

v	λ_v	α	K
500	380.460	0.97667	0.08175
1000	384.480	0.98698	0.0748
1666	386.361	0.99180	0.07209
2000	386.879	0.99314	0.0719
2500	387.401	0.99447	0.0717
5000	388.470	0.99721	0.0717
10000	389.008	0.99859	0.0717
20000	389.279	0.99929	0.0717
50000	389.442	0.99971	0.0717
100000	389.496	0.99985	0.0717
∞	389.55	1.0	0.0717

The dissociation constant of iodic acid is accordingly K = 0.0717.

It is perfectly evident that both of these acids obey the mass law only under certain conditions. The K values do not approach constancy until the degree of dissociation $\alpha \geqq 0.9945$. From the data it is evident that the dilutions, v, at which K becomes a constant, differ in the two acids. It would furthermore appear that the dilutions v are inversely proportional to the dissociation constants, K, of the two acids:

$$\frac{v_{HCl}}{v_{HIO_3}} = \frac{K_{HIO_3}}{K_{HCl}}, \text{ or } v_{HCl} \times K_{HCl} = v_{HIO_3} \times K_{HIO_3}$$

If $\alpha_{HCl} = \alpha_{HIO_3} = 0.9944$, then

$v_{HCl} = 1666$, and $v_{HIO_3} = 2440$ liters.

Therefore $\frac{1666}{2440} = \frac{K_{HIO_3}}{K_{HCl}} = \frac{0.0717}{0.105}$ or

$$1666 \times 0.105\ (= 174.9) = 2440 \times 0.0717\ (= 174.9)$$

If we assume that relationships which hold for strong acids, HX, are also applicable, even if only approximately,

[1] *Ibid.*, p. 2028; see also C. A. Kraus and Parker, *ibid.*, **44**, 2429 (1922).

to strong binary salts, MeX, it would seem worthwhile to determine the dissociation constants of these salts. Let us take the value $\alpha = 0.9953$ for purposes of comparison, because constant K values for binary salts were obtained only beginning with this degree of dissociation. This figure corresponds to a dilution of $v_1 = 2000$ for hydrochloric acid, HCl, or $v_x = 3200$ for iodic acid, HIO_3. For salts of the type of KCl, the corresponding dissociation $\alpha = 0.9953$ when $v_{KCl} = 10000$. We obtain, therefore,

$$(1) \qquad \frac{v_{HCl}}{v_{KCl}} = \frac{K_{KCl}}{K_{HCl}} \text{ or } \frac{2000}{10000} = \frac{K_{KCl}}{0.105}$$

$$\text{or for KCl, } K = \frac{2000 \times 0.105}{10000} = 0.0210$$

$$(2) \qquad \frac{v_{HIO_3}}{v_{KCl}} = \frac{K_{KCl}}{K_{HIO_3}} \text{ or } \frac{3200}{10000} = \frac{K_{KCl}}{0.0717}$$

$$\text{that is, } K_{KCl} = \frac{3200 \times 0.0717}{10000} = 0.0229$$

In general, the dissociation constant, K_x of typical binary salts should be about K = 0.022. This value is in fair agreement with the one obtained by Weiland for potassium chloride, K = 0.020. A value K = 0.0211 was obtained by Bencowitz and Renshaw[1] for trimethyl sulphonium iodide, $S(CH_3)_3I$, at 25° at dilutions v = 11000 to 100000, while the dissociation constant K = 0.0252 was obtained for tri-ethyl sulphonium bromide at dilutions v = 12000 to 100000. In general, a constant K value is obtained in the case of these three binary salts where the degree of dissociation is above $\alpha = 0.996$ and the dilution, v, above 11000–14000. Table X illustrates this point.

We may therefore consider it an established fact that the typical binary salts (halides) which have been examined, obey the mass law in aqueous solutions at dilutions above v = 10000–14000. All of them have a common dissociation constant $K = \frac{\alpha^2}{(1-\alpha)v} \cong 0.02$. This is in

[1] J. Am. Chem. Soc., 47, 1914 (1925).

accord with the inferences made by Washburn,[1] who said, "In sufficiently dilute solution (*i.e.* for most practical purposes below C = 0.0001 N. . .) all univalent salts of strong acids and bases obey the Mass-Action Law and all of them have the same ionization constants."

Table X

Equivalent Conductivities and Dissociation Constants for Trimethyl Sulphonium Iodide, $S(CH_3)_3I$, *at* 25°

Dilution v	λ_v	α	$K = \frac{\alpha^2}{(1-\alpha)v}$
∞	127.49	1.000	
100000	127.434	0.9996	0.0211
50000	127.374	0.9990	0.0211
20000	127.194	0.9976	0.0211
16666	127.134	0.9972	0.0211
12500	127.015	0.9962	0.0212
10000	126.900	0.9953	0.0213
5000	126.400	0.9937	0.02102
2000	125.490	0.9843	0.03033
1000	124.454	0.9762	0.03998

If the above considerations be extended to strong ternary salts of the type MX_2 and if one presupposes that a corresponding state will also be attained when the degree of dissociation $\alpha = 0.9953$, then the dilution, v_x, must be calculated for this value of α. This dilution can be calculated from the formula

$$\lambda_\infty = \lambda_v \left(1 + \frac{0.692 \cdot n \times n'}{v^{0.5}}\right) \text{ or } \alpha = 0.9953 = \frac{v^{0.5}}{v^{0.5} + 0.692 \times 2}$$

We find v = 86000. Since the value $\alpha = 0.9953$ for hydrochloric acid, HCl, corresponds to dilution v = 2000, and since the dissociation constant $K_{HCl} = 0.105$, we may formulate the following proportions

$$\frac{v_{HCl}}{v_{MX_2}} = \frac{K_x}{0.105}, \text{ or } \frac{2000}{86000} = \frac{K_x}{0.105},$$

or
$$K_x = \frac{2000 \times 0.105}{86000} = 0.0024.$$

[1] J. Am. Chem. Soc., 40, 122 and 150 (1918).

Or let us take the binary salt trimethyl sulphonium iodide, $S(CH_3)_3I$. We have $\alpha = 0.9953$ at a dilution $v = 10000$; the constant $K = 0.0211$.
Therefore,

$$\frac{v_{salt}}{v_{MX_2}} = \frac{K_x}{0.0211} \text{ or } \frac{10000}{86000} = \frac{K_x}{0.0211}$$

or $$K_x = \frac{10000 \times 0.0211}{86000} = 0.0024$$

That is, the dissociation constant of a strong ternary salt, MX_2, will be approximately $K_x = 0.0024$.

Let us next compare these dissociation constants of typical strong electrolytes with those of several "weak" or moderately strong organic and inorganic acids.

$$K = \frac{\alpha^2}{(1-\alpha)v}$$

Malonic acid	$CH_2(COOH)_2$	0.00158 (Ostwald 1889)
Maleic acid	$(CH \cdot COOH)_2$	0.012 " "
Dichloracetic acid	$CHCl_2COOH$	0.051 " "
Formic acid	$HCOOH$	0.00023 " "
Selenous acid	H_2SeO_3	0.0040 (Wilcox and Prideaux 1925)
Sulphurous acid	H_2SO_3	about 0.013 (Kerp and Baur 1907)
Nitrous acid	HNO_2	0.00045 (Schumann 1900)

To these may be appended the values found above for "strong" electrolytes

		K
Hydrochloric acid	HCl	0.105
Iodic acid	HIO_3	0.0717
Binary Salts	MX	$\lesssim$ 0.021
Ternary Salts	MX_2	$\leqq$ 0.0024

From the results it is evident that maleic acid, sulphurous acid and the strong binary salts, MeX, have practically the same dissociation constant. Both acids obey Ostwald's law over a wide range of dilutions, and in consequence

thereof, are placed in the class of "weak" electrolytes. Binary salts, on the other hand, being exceptions to Ostwald's law, or obeying this law at the highest dilutions only, are therefore grouped with the "strong electrolytes."

Modern Methods Employed in the Determination of Dissociation Constants

On the basis of our modern conceptions as to the state of electrolytes in solution, a more complicated method is employed for the determination of the dissociation or equilibrium constant, K_0. However, more consistent results, applicable over a wider dilution range, are obtained. Such measurements have been made by Schreiner[1] on acetic and dichloracetic acid. By assuming complete ionization, and taking into account the inter-ionic forces $f\mu$, the viscosity correction η for conductivity values, the activity of water, and the hydration of the hydrogen ion $(H^+ + 8H_2O)$, the following mass-law equation

$$K_0 = \frac{\alpha_0^2 \cdot c}{(1 - \alpha_0)} \cdot \frac{f^2\mu}{a^8_{H_2O}}$$

has been evolved. Ionization of the acid, RCOOH, is represented by the equation

$$RCOOH + 8H_2O \rightleftarrows (H^+ \cdot 8H_2O) + RCOO^-$$

The true degree of dissociation, α_0, includes the old classical degree of dissociation $\alpha = \mu_c/\mu_0$, corrected for the viscosity[2] of the medium η_c/η_0 (that is $\alpha \cdot \eta_c/\eta_0 = \alpha'$), as well as for inter-ionic forces (as expressed by the conductivity coefficient $f\mu$). The value μ_c/μ_0 of totally dissociated hydrochloric acid at the same ion concentration, $\alpha' c_8$, is substituted for $f\mu$. The "true" degree of dissociation is therefore

$$\alpha_0 = \left[\left(\frac{\mu_c}{\mu_0}\right)_{HA} \cdot \frac{\eta_c}{\eta_0}\right] : \left(\frac{\mu_c}{\mu_0}\right)_{HCl} = \frac{\alpha'}{f\mu}$$

For acetic acid at dilutions from 0.0005 to 2.56N, the dissociation constant K_0 was found to equal 1.77×10^{-5},

[1] Z. anorg. Chem., **115**, 186 (1921); **121**, 331 (1922); **122**, 201 (1922).

[2] It may be remembered that a correction for viscosity was used by Ostwald himself in 1888.

(Ostwald in 1887 found $K = 1.8 \times 10^{-5}$); for dichloracetic acid $K_0 = 5 \times 10^{-2}$ (Ostwald found 5.1×10^{-2}). Both the old and new methods gave practically the same dissociation constants for both acids.

A. A. Noyes uses still another method to determine the ionization constants of acids. Complete dissociation, variable ion mobilities, and equivalent conductivities, λ, of the acid from the ionization, γ, are taken into account by the equation $\lambda = \gamma(\lambda_H + \lambda_A)$, where λ_H and λ_A represent the corresponding ion conductivities. The sum $\lambda_H + \lambda_A$ appears in place of λ_∞ in the old formula $\alpha = \lambda/\lambda_\infty$, that is, a value is introduced which is corrected for the decreasing mobility of the ions. This sum is determined for a given ion concentration γc from the equivalent conductivity of the three totally dissociated substances H^+Cl^-, Na^+A^-, and Na^+Cl^- at the same ion concentration. For phosphoric acid at 18°C, the data given in Table XI are obtainable on the basis of the equation

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^-$$

TABLE XI

Molecular Conductivity of the Acid Phosphate Ion

c	NaH_2PO_4	HCl	NaCl	$H^+ + H_2PO_4^- = \lambda_H + \lambda_A$
0.000	70.0	378.3	108.99	339.3
0.001	66.22	375.9	106.49	335.6
0.010	63.86	369.3	101.95	331.2

Thus where $c = 0.001$:

$$\lambda_{HCl} + (\lambda_{NaH_2PO_4} - \lambda_{NaCl}) = 375.9 + (66.22 - 106.49) = 335.6$$

Usual methods[1] are employed for the determination of the activity coefficients or activations of the desired ions at a given ion-concentration γc, e.g. α_H and α_A. If the ionization of electrolytes be designated by γ, that is,

$$\gamma = \frac{\lambda_c}{\alpha_H + \lambda_A},$$

[1] The activity coefficients are a measure of the relation between the activity and the concentration of the ions. Bjerrum regards the determination of the solubilities of salts as the most satisfactory measure of the activity of ions.—See Brönsted and La Mer, J. Am. Chem. Soc., **46**, 555 (1924); Rodebush and Hovorka, *ibid.*, **47**, 1614 (1925).

then the ionization constant may be expressed as

$$K = \frac{\gamma^2 c}{(1 - \gamma)} \alpha_H \alpha_A$$

Table XII gives the data so obtained for phosphoric acid at 18°.

Whereas the K values, as calculated on the basis of the classical dissociation theory (with the aid of α') had always shown an increase with rising concentration c, those obtained by correcting for activation of ions and variance

Table XII

Determination of Ionization Constant of Phosphoric Acid at 18°

c	$\lambda_{H_3PO_4}$	$\alpha' = \lambda/\lambda_0$	$\lambda_H + \lambda_A$	$\gamma = \lambda/\lambda_H + \lambda_A$
0.000	339.3	1.000	339.3	1.000
0.0020	283.1	0.834	335.7	0.843
0.0125	191.2	0.563	332.2	0.575
0.0500	122.7	0.362	327.2	0.375

c	α_H*	α_A	$\frac{(\alpha')^2 c}{(1 - \alpha')}$	$\frac{\gamma^2 c}{1 - \gamma} \alpha_H \alpha_A$
0.000	1.000	1.000		
0.0020	0.958	0.954	0.0084	0.0083
0.0125	0.927	0.908	0.0091	0.0082
0.0500	0.896	0.853	0.0103	0.0086

* Schreiner assumes appreciable hydration of hydrogen ions and takes this into account, but Noyes apparently makes no use of such a factor.

in ion mobilities were found to be practically constant. However, at great dilutions both methods lead to consistent results (K = 0.0084 and 0.0083).

Noyes and Sherrill[1] determined the following ionization constants using this method:

	K
t = 18° phosphoric acid, H_3PO_4 1st hydrogen ion	0.0083
t = 25° sulphurous acid, H_2SO_3 1st hydrogen ion	0.012
t = 25° sulphuric acid, H_2SO_4 for the HSO_4 ion	0.0115

Using the old methods, Kerp and Baur found the dissociation constant for sulphurous acid to be K ~ 0.013,

[1] J. Am. Chem. Soc., 48, 1861 (1926).

while Noyes[1] obtained a value of K = 0.019 for the second step in the dissociation of sulphuric acid. At high dilutions therefore, both methods give for these two acids results which are in fair agreement not only in order of magnitude, but also numerically.

So far as "weak" acids are concerned, it is evident that both the new methods as well as the old Ostwald procedure give K limiting values which are of the same size (provided they do not exceed $K \sim 10^{-2}$).[2]

Can these same relationships be applied to salts? How may the above mentioned "dissociation constants" of binary salts and "strong" mineral acids be interpreted? Can we assume that these "strong" electrolytes at extremely high dilutions may be compared with regard to their ionic dissociation with moderately strong organic acids at dilutions about v = 500-1000, where the modern corrections no longer influence the old values of dissociation constants (Ostwald's values of K)? What value of K shall determine whether an electrolyte is strong or weak?

Let us now consider the views of Bjerrum. Bjerrum delimits the idea of "strong electrolyte" in an altogether different manner. He says, "The typical strong electrolyte is one composed of rigid, unchangeable ions. As worked out in the last few years, the trend of the theoretical views on strong electrolytes has been such as to attempt to explain all properties of electrolytes by aid of interionic forces on the basis of the unchangeability of the ions. . . . In accordance with the most recent views those electrolytes are designated as strong whose ions do not combine measurably with one another under observed conditions. Since the ions of strong electrolytes do not, in general, mutually deform each other, it seems logical to regard as the ideal strong electrolyte that substance composed of non-deformable ions."[3]

The outstanding characteristic of strong electrolytes is here considered to be the *physical condition* of their ions,

[1] Carnegie Institution, Publ. 63, 224 (1907).
[2] See the measurements of Schreiner and of Noyes.
[3] Kgl. Danske Videnskab. Selskab, Math.-fys. Medd., 7 (9), 16, 46 (1926).

which are assumed to be rigid and unchangeable (non-deformable); they may not combine chemically with one another. On the other hand electrical forces at work between the ions of such electrolytes "will in many instances bring about the *association of ions;*" due to inter-ionic forces, oppositely charged ions will tend to approach one another more often than similarly charged or uncharged molecules. Ion pairs will therefore tend to form under certain internal conditions (when, for instance, the sum of the ion radii of water $q \geqq 3.5$ Ångstr.). This introduces a new scientific auxiliary concept viz. the "degree of association." "One can predict that ion association will be large, particularly in the case of small and polyvalent ions. This tendency will presumably also be greater in non-aqueous solvents possessing a small dielectric constant, than it will in water. Association is to be considered as a purely physical process. The existence of this phenomenon would make it more proper to speak not of *100% dissociation*, but of *100% ionization* of strong electrolytes."

This definition may be applied both to dissolved and solid salts. Crystalline potassium chloride is a strong electrolyte. Both in the solid and in the molten state there are systems of the highest degree of association; the ions in the potassium chloride crystal are free only to a very slight extent. A necessary stipulation is, however, "that oppositely charged ions may be in contact with each other without undergoing chemical reaction—that is, forming chemical molecules—or without changing their properties very markedly."

Briefly, "it is not the freedom of the ions which is characteristic of strong electrolytes. . . . On the contrary, their ions may approach each other very closely without causing any noticeable mutual deformation."[1]

What effect will the association of ions have on the conductivity? Bjerrum gives the following explanation: "If there is a decided tendency toward paired association, then the conductivity of the ions will be small. Theoretic-

[1] Bjerrum, Ergebnisse der exakten Naturwiss., **5**, p. 144 (1926).

ally, insolvents with small dielectric constants and at infinite dilutions, the ions will probably be free and unassociated. But even at the lowest concentrations still capable of measurement (0.0001–0.01 molar), association into pairs will still be pronounced and the conductivity small. In more concentrated solutions under such conditions, interionic forces may cause the conductivity to rise with increasing concentration. At higher concentrations the ion pairs will tend to approach more closely to one another; their mutual activity will become less; ternary- and poly-association products will become more frequent, and in consequence of these changes the conductivity will rise. As the concentration becomes greater, a condition is approached which simulates that of fused salts, in which the ions are very strongly associated, not only in pairs. They may, therefore, move and conduct the electric current."

A comparison of the most modern theories with the older views, those which were fostered by the classical dissociation theory, shows many points of contact between them all. The idea of "association" of molecules and ions was used extensively in the old theory, as chemical valencies (residual, molecular, or partial) were considered the cause of associated electrolytes and ions.[1] Ever since Hittorf's experiments with cadmium and zinc halides, transference measurements have brought forth numerous examples of the formation of complex ions. "Intermediate ions" have been shown to exist even in the case of strong electrolytes. Some of these are:

$BaCl_3^-$, $BaBr_3^-$, (Drucker 1913);

$Co(NO_3)_6^{---}$, $CoCl_3^-$, $CoCl_4^{--}$, (Donnan 1912);

Tl_2^{++} in thallous nitrate, $TlNO_3$ (Drucker 1922);

$Ca(SO_4)_2^{--}$ and $SO_4\begin{matrix}\diagup Ca^+ \\ \diagdown Ca^+\end{matrix}$ (Harkins, 1919).

[1] It is a well-known fact that hydration of ions played an important part in the old theories. (Comp. Arrhenius, 1884; Ciamician, Werner, etc.) Modern theories also presuppose such a phenomenon; witness Schreiner's methods for computing the dissociation constants of acids. (See Bjerrum, Z. physik. Chem., 104, 424 (1923); Remy, *Die elektrolytische Wasserüberführung*, Berlin 1927).

Drucker[1] has also emphasized the fact that complex ions exist even in aqueous solutions of typical binary "salts," such as HCl, LiCl, NaCl, and KCl.

Interionic forces exercise a very definite influence, from the modern point of view. High ionic charge and ion concentration, as well as small ionic size and dielectric constants, are all external factors that favor "association." In the last analysis, however, were not "chemical forces" another form of expression for these same electrical forces? Are not valence electrons today used in the same manner as chemical valencies were previously? The old method of thought and reasoning assumed small conductivity to be due to polymerization or association of molecules, and stepwise dissociation or formation of complex ions. Modern theory seeks to find the cause in the association of ions into pairs $(+ \vdots -)$. Heretofore it was thought that the addition of a neutral particle to an electrolyte would increase the ionization and conductivity. Now it is claimed that increased conductivity is the result of an association of higher order to polyionic complexes. Points of approach between both theories are also brought out by thermodynamical treatment of the equilibrium between the free and the associated ions. If αc designates the concentration of the associated substance (where α represents the "degree of association") and $(1 - \alpha)c$ that of the free ions, f′ the activity coefficient of the free ions, application of the law of mass action gives the equation

$$\frac{\alpha c}{[c(1 - \alpha)f']^2} = K \qquad \text{(Bjerrum 1926).}$$

Common principles are involved in this use of the degree of association, α, and that of the degree of dissociation

$$K = \frac{\alpha^2 c}{(1 - \alpha)} \qquad \text{(Ostwald's equation)}$$

Bjerrum's new association theory of "strong" electrolytes is, in my opinion, an advance and a valuable line

[1] Z. physik. Chem., **111**, 32 (1924).

of thought since it regards the association products not as chemically combined, undissociated molecules, but as paired ions which retain the essential properties of ions.

SUMMARY

The classical theory of electrolytic dissociation has created the terms "strong" and "weak" electrolytes (salts, acids and bases). The equivalent electrical conductivities, λ_v, of aqueous solutions at moderate dilutions, v, and at temperatures about 18°C, have been used to distinguish between the two groups. "Strong" electrolytes are good conductors; that is, they have high numerical λ_v-values. The uni-univalent strong salts have, in general, an average numerical λ-value of about 100, the strong bases, about 200, the strong acids, about 300. Increase of dilution, ranging from $v = 10$ to 100 to 1000 liters, causes only a relatively slight increase in equivalent conductivity values. Therefore, it had been assumed that in these solutions strong electrolytes approached a high degree of ionic dissociation, since free ions are carriers of electricity and the relation between the conductivity λ_v at the given dilution v and the conductivity λ_∞ at the infinite dilution $v = \infty$, was nearly unity, that is $\lambda_v/\lambda_\infty \leqq 1$. This conductivity coefficient $\alpha = \lambda_v/\lambda_\infty$ is called the "degree of dissociation."

For general purposes of classification of different kinds of electrolytes, the old terms "strong" and "weak" still retain their value today. Conductivity data thus offer a characteristic mark for the qualitative recognition of "strength." The problem of the quantitative determination of the "degree of dissociation" and the question of the "dissociation constants" are quite different matters. With regard to these problems we are in a position better to appreciate the bitter words of W. D. Bancroft (1926): "Forty years of intensive development have brought to us the point where we cannot determine any electrolytic dissociation with any degree of accuracy and where we question the significance of the term 'electrolytic dissociation'."

Our classical views have been of exceptional use throughout these four decades. If the comparison is permissible, they have been durable scientific crutches by whose aid the investigator has been able to go a long way on the road to progress in the new land of the natural sciences. Now we are to do away with these old supports; it is said that they were not built staunchly and exactly enough. We are asked to find new ones! In the meantime we have lost faith in the old ones, and have been trying continually to use the new ones, which are not, however, suitable for the rapid strides of progress.

CHAPTER VIII

Conductivity Curves of Non-aqueous Salt Solutions in Accordance with the Square-root Law

> "In general, in the case of non-aqueous solvents the data (i.e. of ionization) are so meagre and in some cases so conflicting that no definite statements can be made about them at the present time."
>
> —W. C. McC. Lewis.[1]
>
> "No one disputes that we are very far from being clear as to the physical chemistry of non-aqueous solvents."
>
> —W. D. Bancroft.[2]

THESE two pessimistic statements are placed appropriately at the beginning of this chapter. May they serve as powerful stimulants for further experimental researches, for a rich scientific harvest awaits accurate investigation in this wide and productive field of study!

GENERAL DISCUSSION

In 1868, at the very beginning of his investigations on the conductivity of aqueous solutions, Kohlrausch stated that zinc sulphate in solution "was the only decomposable conductor whose resistance had been studied adequately." Progress since then, for the last half century, is due chiefly to two apparently inconsequential manipulative changes; first, the use of alternating in the place of direct current; secondly, the use of the Bell telephone (1876) as a zero instrument.

The importance of the Bell telephone for the making of conductivity measurements has been suitably emphasized by Kohlrausch: "A new era for experimentation dawned with

[1] *A System of Physical Chemistry*, II, 223 (1925).
[2] J. Am. Chem. Soc., Golden Jubilee Number, 48, 108 (1926).

the introduction of the Bell telephone. . . . The telephone has made the determination of electrical conductivity one of the simplest of tasks, and [since 1880] this method has been rapidly extended."[1]

Friedrich Kohlrausch, the physicist, has unquestionably rendered a great service in this field of research. Beginning in 1869 he studied, during the next forty years, the electrical conductivity of *solutions* of electrolytes. He investigated the typical binary and ternary inorganic salts as well as several inorganic acids and bases. We are indebted to him (1) for the introduction of the concepts "molecular and equivalent conductivity," (2) for the law of the independent mobility of ions (1876, 1879), (3) the square-root law for the extrapolation of the maximal conductivity at zero concentration (1900), and (4) for the calculation of ion mobilities at infinite dilution and 18° ($\lambda_\infty = u_0 + v_0$).

So far as Kohlrausch was concerned, all of his methods, purposes and results were considered from the physicist's point of view. Arrhenius and W. Ostwald were responsible for studying the electrical conductivity of electrolytes in aqueous solution from the point of view of chemical relationship, chemical structure and electrolytic dissociation.

The classical dissociation theory of Arrhenius ushered in a new era for conductimetric investigations, involving problems of a highly varied nature. Water was still used as solvent, but the chemical nature and constitution of the substances investigated varied extremely. Countless numbers and varieties of organic acids and their salts (W. Ostwald and co-workers), organic bases and their salts (Bredig), and polyvalent inorganic electrolytes (up to the highest temperatures by A. A. Noyes and co-workers) were added to the classic determinations for the simpler inorganic substances.

Non-aqueous solutions at first were not investigated. This neglect was chiefly due to the theory of dissociation itself. Noted champions of this theory assumed as late as 1891, that ionization of acids, bases and salts was lacking

[1] Z. Elektrochem., **14**, 384 (1908).

altogether in alcoholic solutions.[1] In 1893 W. Ostwald[2] wrote that water, in so far as its ability to form electrolytic solutions or to cause ionization was concerned, stands in a class by itself, a position "which is not even approximately simulated by any other substance."

Not until 1892 was there a visible change in theoretical opinions and experimental interest with reference to non-aqueous substances as ionizing solvents. The alcohols were the first solvents to be investigated,[3] followed by the fatty acids,[4] and the ketones.[5] Kahlenberg and Lincoln (1899) studied the aldehydes, esters, and cyclic bases. These investigations became increasingly extensive and more classes of organic media were investigated as solvents. Nevertheless the results obtained were relatively of little value for several reasons: (1) The electrolytes were chosen with special regard to their solubility and often were unsuited for observational purposes, since substances like $HgCl_2$, $FeCl_3$, $SbCl_3$, and $AsCl_3$, are either weak, or unstable electrolytes; (2) The conductivity measurements were often limited to a very narrow dilution range, rendering impossible a true evaluation of the λ,v-curve and of the degree of dissociation $\alpha = \lambda_v/\lambda_\infty$; (3) The numerical values for the conductivity, λ_v, can be regarded as only first approximations, since questions concerning the purity of solute and solvent were not then sufficiently taken into consideration. This first period in the study of non-aqueous solvents is mainly a period of search for suitable ionizing solvents among the various classes of organic compounds. Taking the numerical relations of aqueous solutions as a prototype, greater or lesser conductivity was regarded as the chief criterion for the ionizing tendency of the individual solvents and for the dissociation of the investigated substances.

Toward the end of the last century two quite unique and simply constituted inorganic solvents were

[1] van Deventer and Reicher, Z. physik. Chem., **5**, 177 (1890); **8**; 536 (1891).

[2] *Lehrbuch der allgemeine Chemie*, II (1), 205, 799 (1893).

[3] Völlmer (1892), Holland (1893), Schlamp (1894), and Carrara (1894) are the pioneers in this field.

[4] Jones (1894); Zanninovich-Tessarin (1896).

[5] Carrara (1895); Dutoit and Aston (1897).

added to the list of inorganic ionizing media. Liquid ammonia, found by Cady (1897) to be a dissociating solvent, was thoroughly investigated by Franklin and Kraus, partly in co-operation, also individually during 1899–1909. Numerous substances were investigated by them even to greatest possible dilutions and to the highest feasible temperatures.

The other solvent, acid in nature compared with basic ammonia, was liquid sulphur dioxide, discovered and studied in a preliminary fashion by Walden in 1899. In 1901 it was subjected to thorough experimental investigation at temperatures from $t = -67°$ to $+158°$ (critical temperature) by Walden and Centnerszwer. Other inorganic ionizing solvents were developed as result of the researches of P. Walden (1900-1902, SO_2Cl_2, $SOCl_2$, $POCl_3$, H_2SO_4, etc.), Lewis and Wheeler (1906, liquid iodine as a solvent for potassium iodide), and Archibald, McIntosh and Steele (1904–05, 1907, liquid hydrogen chloride, hydrogen bromide and hydrogen iodide, as solvents for organic compounds). While the above investigations helped to extend the field of pure organic and inorganic solvents, H. C. Jones (and his co-workers, Lindsay, Carroll, Bassett, Bingham, McMaster, Rouiller, Veazey, Davis, Putnam, Mahin, Guy, Getman, Schmidt, and others, 1902–1916) undertook to study mixed solvents.

It is very gratifying, indeed, that the last decade has resulted in the production of a whole series of precise conductivity measurements of non-aqueous solvents. Space permits the mention of only a few of the most indefatiguable workers in this field: Goldschmidt (in Oslo) who employed principally alcohols as solvents; Kraus and his co-workers, as well as Hartley and Frazer (1925) who also used the alcohols (methyl alcohol, etc.); Getman (1914) who studied furfurol solutions; Philip and Oakley (1924) who investigated nitromethane; and Creighton and Way (1918-19) who made comparative studies of a whole group of solvents.

A quarter of a century ago Walden began a systematic investigation of organic solvents and ionizing media, which has been continued up to the present time.[1]

The purposes and aims of these investigations may be summarized briefly:

(1). To study a large number and variety of solvents with the aid of one or very few typical binary salts.

(2). To determine the conductivities, λ_v, for each individual solvent over a wide dilution-range and at various temperatures.

(3). To extrapolate the maximal conductivities, λ_∞, by a uniform procedure, so as

(4). To draw conclusions from the degree of dissociation, $\alpha = \lambda_v/\lambda_\infty$, as to the "ionizing power" of the solvent under investigation,

(5). To link this ionizing power numerically with the dielectric constant, ϵ, of the solvent.

(6). To bring the conductivity values, λ_v, and the maximal conductivity, λ_∞, into a definite relation with the viscosity, η, of the solvent.

(7). To determine the ion mobilities from the maximal conductivity λ_∞. Then

(8). To vary the number and constitution of the salts, as each of the above working hypotheses gave promise of success, and at the same time

(9). To study solvents with reference to their ionizing powers—even so-called "non-conductors."

(10). To determine the molecular weights of salts in different ionizing solvents.

No one will deny that it is impossible for any one man, in the course of a few years, to bring to satisfactory completion a program such as the one outlined above. Naturally the personal element enters into work of this sort. During the years in which these studies have been carried on, the methods of procedure have been developed

[1] The first article appeared in Z. physik. Chem., **46**, 103 (1903); the most recent, *ibid.*, **123**, 429 (1926).

to such an extent that much of the earlier work, in spite of all precautionary measures, was found to possess only a qualitative value and to be useful only for purposes of orientation.

The following chapters will be devoted to a discussion of several important questions concerning the conductivity of salts, in the main the simple uni-univalent salts of the type MX, in non-aqueous solvents. In so far as the results make it possible, an attempt will be made to find solutions for these problems. In addition to the alkali halides, will be considered among the typical binary salts the alkylated ammonium salts. The latter were investigated in order to throw light on the influence of the chemical nature and of the size of the cations M^+ and anions X^- of a given type of salt. The behavior of these simple and typical electrolytes in water was used as a standard of comparison for investigations that included solutions of these substances even in the so-called "non-conductors" of the hydrocarbons.

Chief stress was laid upon the determination of the maximal conductivity λ_∞ (at infinite dilution, $v = \infty$), in order to secure uniform bases for the calculation of the "classical" degree of dissociation $\alpha = \lambda_v/\lambda_\infty$. It was hoped that these values for α would make it possible to compare the behavior of the chosen salts in water as solvent.

Proof of the Square-root Law

Let us first demonstrate the validity of the square-root formula by graphic presentation of data obtained under the most precise experimental conditions on a series of typical binary uni-univalent salts. Careful examination of these will show that extrapolation of the limiting conductivity, λ_∞, as based on present-day theoretical considerations and experimentally possible conditions, leads to uniform numerical values.

Bredig's measurements of the conductivities of binary (alkylated ammonium) salts in water, for dilution range $v = 32$–1024 are given in the form of curves in Fig. 1.

Figure 2 shows the conductivities in methyl alcohol at 25° as measured by Frazer and Hartley in 1925, for dilution ranges of v = 500–10000.

Figures 3 and 4 show the conductivity curves in ethyl alcohol and ammonia.

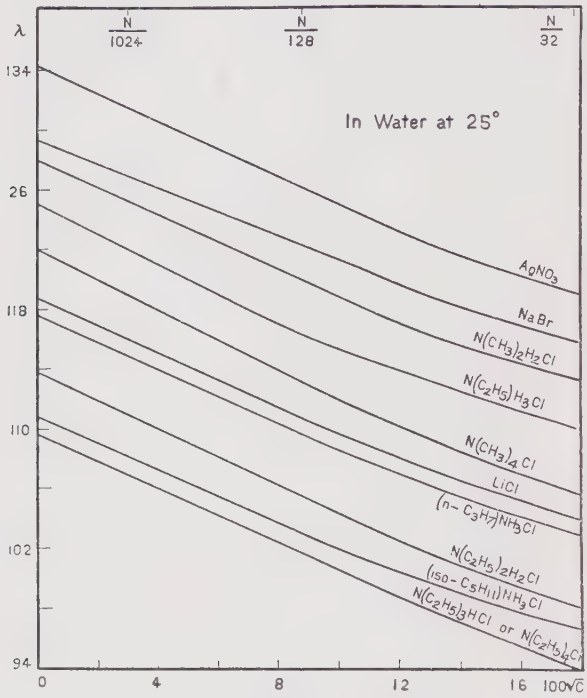


FIG. 1

Figure 5 depicts the conductivities of various salts in acetone solution at 25°C. The curves are obtained by plotting the conductivity values, λ_v, as the ordinates and the corresponding $\sqrt{c}$ values as the abscissae. From the diagram $\lambda - \sqrt{c}$ it will be evident that the curves of the individual salts show considerable variation in slope (the tangents a of the inclination of the limiting right lines $\lambda_v = \lambda_\infty - a\sqrt{c}$ will be considered in more detail later on).

Tetra-ethylammonium styphnate, a uni-bivalent salt, is distinguished by the extreme steepness of its curve. Diethylammonium chloride and isobutylammonium chloride apparently also belong to a different class of salts—that is,

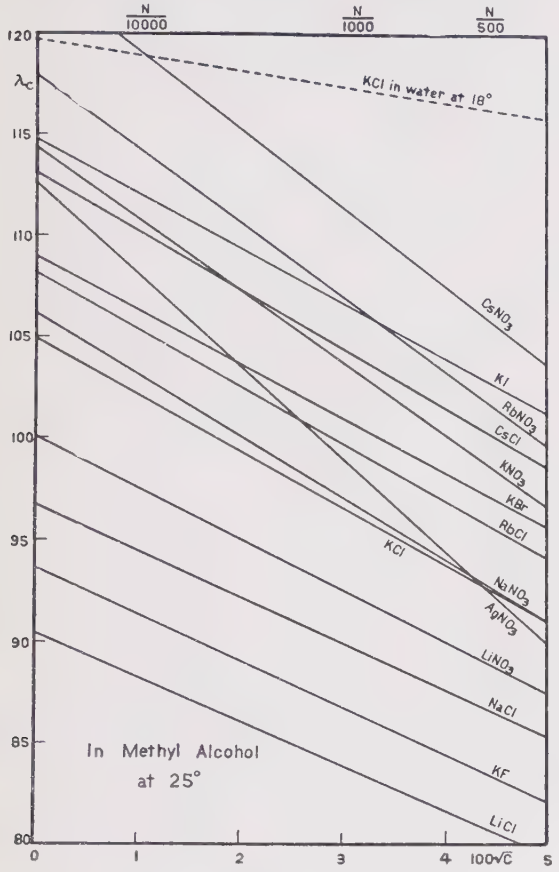


FIG. 2.

	λ_0 at 25°
LiCl	90.90
NaCl	96.95
KCl	105.05
RbCl	108.65
CsCl	113.60
KF	94.0
KBr	109.35
KI	114.95
NH_4Cl	111.00
HCl	193.5
$LiNO_3$	100.25
$NaNO_3$	106.45
KNO_3	114.55
$RbNO_3$	118.15
$CsNO_3$	122.95
$AgNO_3$	112.95
NaBr	101.5
$NaOCH_3$	98.40
$NaClO_4$	115.10

are extremely weak electrolytes—judging from the strikingly small values of λ and the flatness of their curves.

Figure 5 shows the conductivities in acetone at 25°C.

It can be proved that typical strong salts with large, non-solvated, ions follow the square-root law at dilutions from $v = 2000$ liters per mol and upwards.

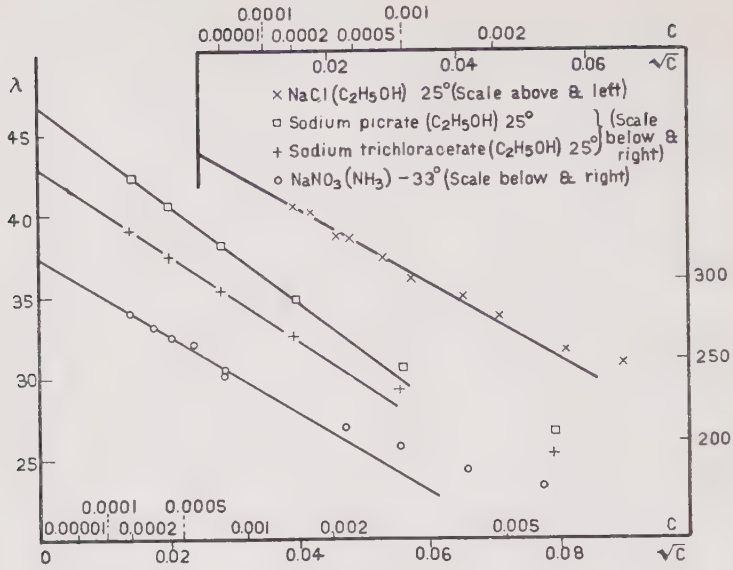

0.0001
0.00001 0.0002 0.0005
0.001
0.002
C
0.02
0.04
0.06
√C
× NaCl (C2H5OH) 25° (Scale above & left)
□ Sodium picrate (C2H5OH) 25°
+ Sodium trichloracetate (C2H5OH) 25° (Scale below & right)
○ NaNO3 (NH3) −33° (Scale below & right)
λ
45
40
35
30
25
300
250
200
0.0001
0.0005
0.00001
0.0002
0.001
0.002
0.005
C
0
0.02
0.04
0.06
0.08
√C

FIG. 3

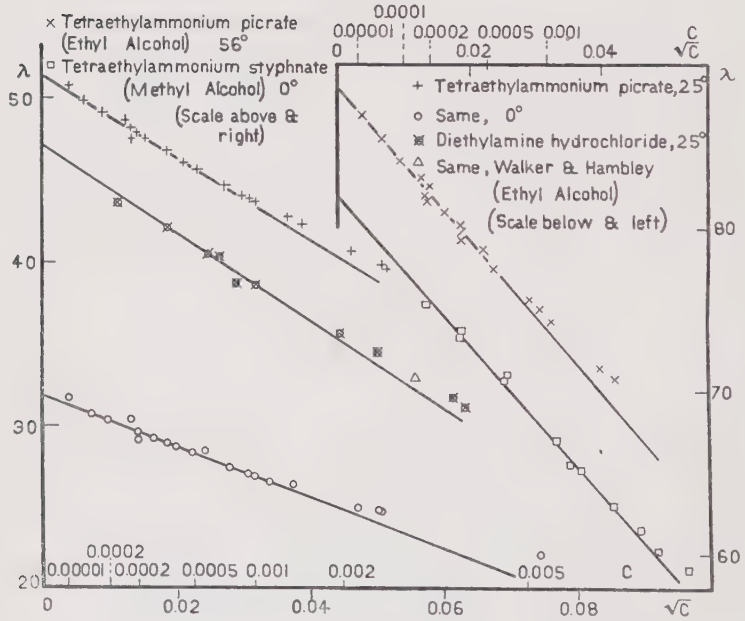

× Tetraethylammonium picrate (Ethyl Alcohol) 56°
□ Tetraethylammonium styphnate (Methyl Alcohol) 0°
(Scale above & right)
0.0001
0.00001 0.0002 0.0005 0.001
0
0.02
0.04
C
√C
+ Tetraethylammonium picrate, 25°
○ Same, 0°
⊠ Diethylamine hydrochloride, 25°
△ Same, Walker & Hambley (Ethyl Alcohol)
(Scale below & left)
λ
50
40
30
20
80
70
60
0.0002
0.00001 0.0002 0.0005 0.001
0.002
0.005
C
0
0.02
0.04
0.06
0.08
√C

FIG. 4

Table XIII gives the figures obtained and those required by theory for tetra-ethylammonium picrate, $N(C_2H_5)_4^+ \cdot [OC_6H_2(NO_2)_3]^-$ at 25°C, assuming the values for $\lambda_\infty = 177.3$ and $a = 954.2$ as obtained by the method of least squares.

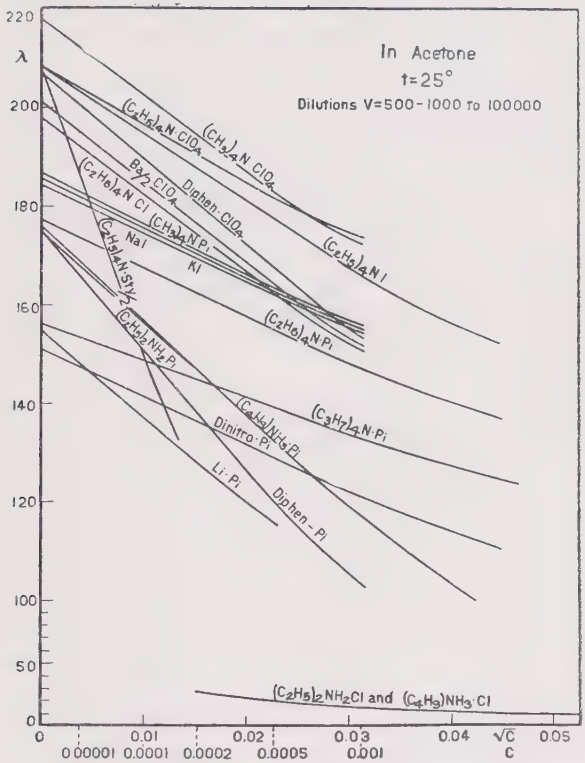


FIG. 5

The a and a/λ_∞ values, for the various salts, noted in Table XIV are obtained by evaluation of the λ_∞ limiting conductivities using the square-root formula $\lambda_\infty - \lambda_v = a\sqrt{c}$.

From the values given in Table XIV for uni-univalent salts it is evident that there are three distinct groups which differ from one another by the size of the quotient a/λ_∞: [See bottom of p. 209].

TABLE XIII

Proof of the Square Root Formula

$N(C_2H_5)_4 \cdot OC_6H_2(NO_2)_3$ in Acetone

$v = 1/c$	λ_v determined	λ_v calculated	Diff.
55240	173.5	173.3	+0.2
30120	171.8	171.8	0.0
25090	171.3	171.3	0.0
16910	170.0	170.0	0.0
10600	168.0	168.0	0.0
8969	167.4	167.3	+0.1
3869	162.0	162.0	0.0
3027	159.9	159.9	0.0
2134	156.5	156.6	−0.1
1557	153.3	152.8	+0.5
622.7	141.5	139.1	+2.4

TABLE XIV

Constants Obtained From Conductivity Curves

No.	Salts	t	λ_∞	a	a/λ_∞
1	Tetrapropylammonium picrate	25	156.6	730	4.66
2	Tetra-ethylammonium picrate	0	141.4	810	5.73
		25	177.3	954	5.38
		50	218.6	1230	5.62
3	Potassium iodide	0	147.8	787	5.33
		25	185.6	977	5.27
		50	229.2	1200	5.24
4	Sodium iodide	0	145.0	752	5.19
		25	184.5	980	5.31
		50	227.4	1220	5.37
5	Dinitrophenylpyridinium picrate	0	120.5	810	6.72
		25	151.5	980	6.47
		50	186.5	1220	6.54
6	Tetra-methylammonium picrate*	0	148.7	822	5.46
		25	187.0	1020	5.46
		50	229.4	1273	5.54

*The salts 6, 13, and 14 are isomeric salts.

TABLE XIV (continued)

Constants Obtained From Conductivity Curves

No.	Salts	t	λ_∞	a	a/λ_∞
7	Tetra-ethylammonium perchlorate	0	166.5	923	5.54
		25	208.7	1160	5.56
		50	256.0	1430	5.59
8	Tetra-ethylammonium iodide	0	166.3	1020	6.13
		25	209.0	1340	6.42
		50	256.2	1700	6.63
9	Tetra-ethylammonium chloride	0	158.1	1240	7.84
		25	198.1	1550	7.83
		50	242.4	1910	7.88
10	Tetra-ethylammonium perchlorate	25	218.5	1550	7.09
11	Diphenyl guanidine perchlorate	25	207.3	1730	8.35
12	Lithium picrate	0	123.6	1420	11.5
		25	155.0	1760	11.4
		50	191.0	2170	11.4
13	Diethylammonium picrate*	25	175.6	1890	10.8
14	Isobutylammonium picrate*	0	140.8	1530	10.9
		25	176.6	1930	10.9
		50	217.6	2410	11.1
15	Diphenyl guanidine picrate	25	176.0	2420	13.8
16	Diethylammonium chloride	25	Slopes for curves of these two salts could not be determined.		
17	Isobutylammonium chloride	25			
	Dibasic Salts				
18	Barium perchlorate	0	160.9	1330	8.27
		25	201.2	1600	7.95
		50	248.2	2360	9.51
19	Tetra-ethylammonium styphnate	0	165	4400	26.7
		25	208	5800	27.9
		50	256	7500	29.3

*The salts 6, 13, and 14 are isomeric salts.

First, that group of salts for which $a/\lambda_\infty = 5 - 6.5$. These include the strong binary salts such as potassium and sodium iodides and the tetra alkylated ammonium salts.

Secondly, that group where $a/\lambda_\infty \sim 11$, approximately double the value of those in the first, which includes the lithium, di-ethylammonium and isobutylammonium picrates.

Thirdly, the chlorides of the last-mentioned bases, the a values of which are experimentally undeterminable in

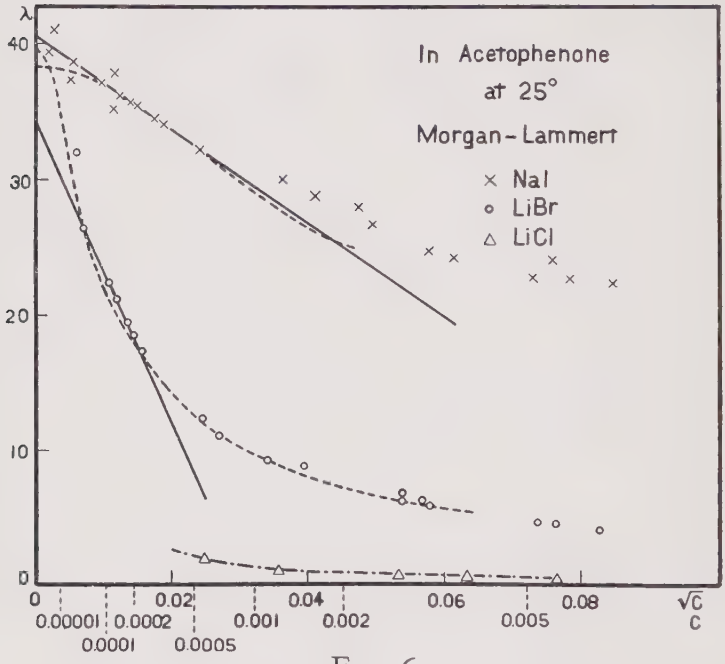


FIG. 6

view of the fact that the conductivity values are so greatly retarded.

The quotient a/λ_∞ is constant in each group for temperatures between 0° and 50°, whereas a shows considerable variation. On the other hand it should be noted that $a \sim 1000$ at 25° in the case of the first group, which includes the alkali and tetra-alkylated ammonium salts at 25°. This was to be expected from the Walden d_v-formula used in the calculation of the limiting values, as $a = K/\epsilon \cdot \eta = 982$. From this formula it follows that $a \sim 1/\eta$. If, as is generally

the case, $\lambda_\infty \cdot \eta$ can be made a constant, then a/λ_∞ (a value independent of temperature) may be expressed as $a \sim 1/\eta$.

Appreciable irregularities become apparent when acetophenone is used as solvent. At higher concentrations the λ_v-values for the three typical salts, NaI, LiBr and LiCl,

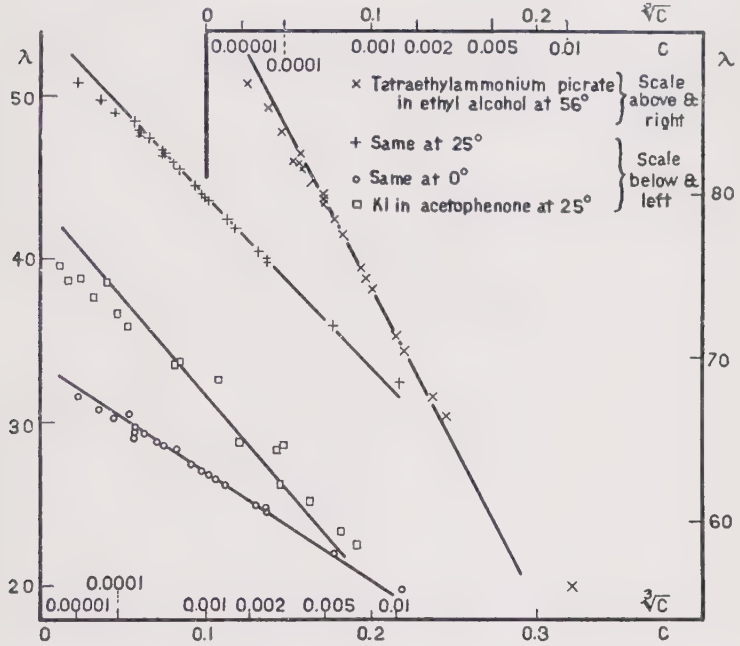


FIG. 7

vary considerably, such that the last mentioned salt would appear to be a "weak" electrolyte. Thus,

NaI		LiBr		LiCl	
c	λ_v	c	λ_v	c	λ_v
0.06324	13.08	0.06005	1.743		
0.005264	23.27	0.005409	4.838	0.005616	0.6141

Where v ~ 1800, the respective λ_v-values stand in the ratio

$$23.27 : 4.838 : 0.6141$$

Disregarding the observations made at great dilutions,

Morgan and Lammert[1] have treated the λ-values from the standpoint of the law of mass action. Their results are plotted in Fig. 6. The solid (straight) lines have been drawn in by Walden on the basis of the $\sqrt{c}$ formula.

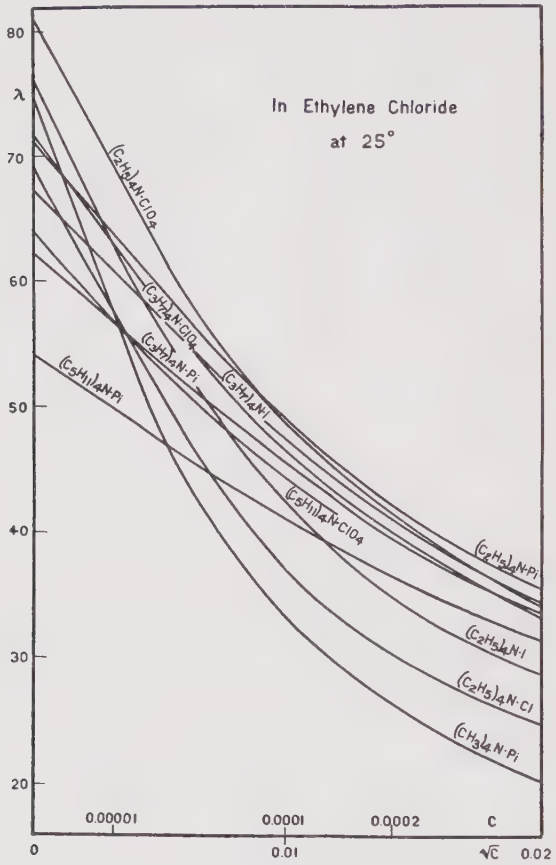


FIG. 8

All of the data in Figs. 6 and 7 have been based upon the use of the square-root formula. Fig. 6 shows a number of curves in which the data are calculated by the cube-root formula.

[1] J. Am. Chem. Soc., 46, 1126 (1924).

Figure 7 shows the conductivity curves in ethyl alcohol and acetophenone as calculated by the $\sqrt[3]{c}$ formula.

From Figure 7 it is clear that the straight lines based on the $\sqrt[3]{c}$ formula do not agree, at dilutions where $v \geqq 10000$ liters, with the experimental data. They are high and would lead to higher values for the maximal conductivities λ_∞.

Figure 8 illustrates the behavior of binary salts in a hydrocarbon, ethylene chloride, $CH_2Cl{\cdot}CH_2Cl$. The data from which the curves are drawn are computed by the square-root formula.

TABLE XV

Proof of the Square-root Law in Ethylene Chloride, $t = 25°$

Salt: Tetra-ethylammonium picrate, $N(C_2H_5)_4{\cdot}OC_6H_2(NO_2)_3$ (The values $\lambda_\infty = 71.26$ and $a = 2330$ are substituted in the formula $\lambda_v = \lambda_\infty - a\sqrt{c}$).

$v = 1/c$	λ Found	λ Calculated	Δ Difference
190700	65.81	65.93	−0.12
104000	64.19	64.06	+0.13
70130	62.41	62.45	−0.04
60610	61.82	61.80	+0.02
38110	59.22	59.33	−0.11
23230	55.94	56.00	−0.06
20030	54.82	54.79	+0.03
19540	54.77	54.60	+0.17
17260	53.73	53.53	+0.20
15780	53.13	52.71	+0.42
13910	51.98	51.50	+0.48
8264	47.03	45.63	+1.40
4505	41.30	36.54	+4.76
2243	34.59	22.05	+12.54
1246	29.38	5.25	+24.13

In Table XV the agreement between the directly measured λ-values and those calculated is excellent within the dilution range $v = 190000$ to 20000 liters. Below the latter dilution value, the determined and calculated values begin to diverge and at $v = 1245$, no conformity at all is evident.

In the case of solutions of tetraproplyammonium picrate in tetrachlorethane (dielectric constant $\epsilon = 8.15$), the square-root law begins to be applicable at v = 37000 liters.

TABLE XVI

Proof of the Square-root law in Tetrachloroethane, $C_2H_2Cl_4$, t = 25°

Salt: Tetrapropylammonium picrate, $N(C_3H_7)_4 \cdot OC_6H_2(NO_2)_3$ (The values $\lambda_\infty = 30.3$ and a = 2593 are substituted in the square-root formula.)

v = 1/c	λ Found	λ Calculated	Δ Difference
385930	26.15	26.1	+0.05
268990	25.3	25.3	0.0
210020	24.42	24.6	−0.18
175420	23.9	24.1	−0.20
135050	23.1	23.2	−0.10
85206	21.36	21.4	−0.04
72015	20.6	20.6	0.0
64321	20.0	20.1	0.1
55721	19.4	19.3	+0.1
42804	17.8	17.8	+0.0
35787	16.9	16.6	+0.3

SUMMARY

Examination of the validity of the square-root law, $\lambda_v = \lambda_\infty - a\sqrt{c}$ for typical binary (uni-univalent) salts in non-aqueous solvents by graphic and mathematical procedures has led to the following results:

Solvent (t = 25°)	Salts	Validity of law begins at a dilution of v =	Dielectric constant of solvent ϵ	v = $\left(\frac{270}{\epsilon}\right)^3$
Methyl alcohol	$N(C_2H_5)_4$ picrate	>500	32–34	600–500
Ethyl alcohol	" "	1400	24	1420
Acetone	" "	2100	21	2120
Acetophenone	KI, NaI	>2100	18	3300
Ethylene chloride	$N(C_2H_5)_4$ picrate	20000	10	19700
Tetrachloroethane	$N(C_3H_7)_4$ "	37000	8.1	37000
Water			80	38–39

The square-root formula is valid for all solvents investigated thus far, but its application is dependent upon the

dielectric constant ϵ of the solvent. The smaller the value for ϵ, the higher will be the dilution range at which the λ,v-curve will begin to approximate a straight line. The calculated values for $v = (270/\epsilon)^3$ given in the last column of the above table show a satisfactory agreement with the v-values at which the square-root formula becomes valid. The empirical equation $v = (270/\epsilon)^3$ offers a means for predicting this characteristic dilution, provided tetraethyl- or tetrapropylammonium picrates are employed. Applying this equation to benzene and chloroform the following results are obtained:

Chloroform: $v = (270/4.95)^3 = 162000$ liters

Benzene: $v = (270/2.19)^3 = 1870000$ liters.

In other words, the square-root formula for strong binary salts would become valid in these solvents at dilutions $v \sim 200000$ and 2000000 liters respectively.

CHAPTER IX

Numerical Data of Conductivity and Degree of Dissociation in Water, Methyl and Ethyl Alcohols, and Acetone

Empirical rules for the calculation of the maximal conductivities and the classical degree of dissociation for strong electrolytes (salts)

In the following pages it will be demonstrated that, in view of the fact that strong typical binary salts dissociate in a similar manner, empirical rules can be set up which make possible the rapid calculation of the limiting values λ_∞ and the "degree of dissociation" $\alpha = \lambda_v/\lambda_\infty$

1. Aqueous solutions

(a) Calculation of the limiting value λ_∞ by the Ostwald-Walden-Bredig Rule at 25°.

$$dv = (\lambda_\infty - \lambda_v) = \frac{K}{\epsilon \cdot \eta \cdot v^{0.5}}, \text{ and } \lambda_\infty = \lambda_v + d_v.$$

$$\text{For water } d_v = \frac{65.7}{80 \times 0.00891 \times v^{0.5}} = \frac{92.17}{v^{0.5}}$$

Trimethyl Sulphonium Iodide (Bencowitz-Renshaw), t = 25°

v = 1/c	dv calc.	λ_v found	λ_∞ calc.	Calculated $\lambda_v = (127.76 - d_v)$	Difference λ_v fd − λ_v cal
2 000	2.061	125.49	127.55	125.50	−0.01
5 000	1.303	126.40	127.70	126.46	+0.06
10 000	0.922	126.90	127.82	126.84	+0.06
12 500	0.824	127.01	127.83	126.94	+0.07
20 000	0.652	127.19	127.84	127.11	−0.08
26 720	0.564	127.26	127.82	127.20	−0.06
50 000	0.412	127.37	127.77	127.35	−0.02
100 000	0.291	127.43	127.72	127.47	+0.04
∞		127.76	127.8	(127.76)	

(b) Calculation of the limiting value λ_∞ in aqueous solutions by the formula $\lambda_\infty = \lambda_v \left(1 + \frac{0.692}{v^{0.5}}\right)$

Potassium chloride, KCl, (Weiland's measurements),[1] t = 18°.

Dilution v =	1000	2000	5000	10000
λ_{found} =	127.25	128.05	128.68	129.03
$\lambda_{\infty\,calc}$ =	130.0	130.0	129.92	129.90
By formula (a) =		130.1	129.98	129.95

Dilution v =	20000	50000	100000	∞
λ_{found} =	129.32	129.51	129.57	129.64
$\lambda_{\infty\,calc}$ =	129.95	129.91	129.86	129.94
by (a) =	129.97	129.92	129.86	129.96

The maximal conductivity for potassium chloride, as calculated by means of the square-root formula from the most reliable λ-values (Kohlrausch; Weiland), has been found by various investigators to be:

λ_∞ = 130.00 (Debye and Hückel, 1923)
129.98 (Szyszkowski, 1926)
129.93 (Landolt-Börnstein Tables, 1927)

Trimethyl sulphonium iodide, $S(CH_3)_3I$, (Bencowitz and Renshaw),[2] t = 25°

v =	5000	10000	12500	26720
λ_{found} =	126.40	126.90	127.015	127.259
$\lambda_{\infty\,(calc.}$ =	127.74	127.78	127.80	127.79

v =	50000	100000	∞
λ_{found} =	127.374	127.434	127.49 (or 127.76)
$\lambda_{\infty\,calc.}$ =	127.77	127.71	127.8 (or 127.75)

Using the $\sqrt{c}$-formula and by extrapolation, these two investigators[3] have found λ_∞ = 127.76, a value identical with that calculated by Walden.

[1] J. Am. Chem. Soc., **40**, 146 (1918).
[2] J. Am. Chem. Soc., **47**, 1914 (1925).
[3] Bencowitz and Renshaw, J. Am. Chem. Soc., **48**, 2152 (1926).

TABLE XVII
Uni-univalent Salts at t = 0° *and* 18°

	v =	100	200	500	1000	2000	5000	δ I	δ II
				$NaNO_3$					
t = 18°	λ_v =	98.2	100.1	100.9	102.9	—	—	*105.1*	*105.25*
	λ'_∞ =	105.0	105.0	105.05	105.15	—	—	*105.05*	
				$CsNO_3$					
t = 0°	λ_v =	78.6	80.3	81.8	82.5	83.1	—	*84.4*	*84.35*
	λ'_∞ =	84.03	84.24	84.35	84.31	84.39	—	*84.3*	
				$KClO_3$					
t = 0°	λ_v =	—	—	73.5	74.4	74.9	—	—	—
	λ'_∞ =	—	—	75.8	76.03	76.06	—	*76.0*	—
t = 18°	λ_v =	111.6	113.8	115.8	116.9	117.7	—	*119.4*	*119.55*
	λ'_∞ =	119.35	119.35	119.40	119.40	119.50	—	*119.4*	
				KCl					
t = 0°	λ_v =	77.4	78.5	79.7	80.3	80.8		*81.8*	*81.95*
	λ'_∞ =	82.7	82.36	82.19	82.06	82.06		*82.1*	
t = 18°	λ_v =	122.4	124.4	126.3	127.4	128.1	128.8	*129.8*	*129.85*
	λ'_∞ =	130.8	130.5	130.1	130.2	130.1	129.8	*130.0*	

TABLE XVII (continued)
Uni-univalent Salts at t = 0° *and* 18°

				KNO_3					
t = 0°	λ_v =	75.7	77.2	78.4	79.0	79.4	—	*80.5*	*80.55*
	λ'_∞ =	80.9	80.9	80.85	80.72	80.63	—	*80.7*	
t = 18°	λ_v =	118.2	120.5	122.6	123.7	124.5	125.2	*126.2*	*126.35*
	λ'_∞ =	126.4	126.4	126.4	126.4	126.4	126.2	*126.35*	
				$KClO_4$					
t = 0°	λ_v =	72.7	74.1	75.4	76.0	76.4	—	*77.6*	*77.4*
	λ'_∞ =	77.71	77.71	77.71	77.66	77.60	—	*77.68*	
t = 18°	λ_v =	114.2	116.6	118.7	119.9	120.8	—	*122.8*	*122.75*
	λ'_∞ =	122.1	122.3	122.4	122.4	122.7	—	*122.5*	
				$LiClO_4$					
t = 0°	λ_v =	51.6	52.6	53.4	53.8	54.1	54.4	*54.8*	*54.95*
	λ'_∞ =	55.16	55.18	55.06	54.98	54.95	54.92	*54.95*	
t = 18°	λ_v =	83.1	84.7	86.3	87.0	87.5	88.0	*88.8*	*88.9*
	λ'_∞ =	88.84	88.85	88.98	88.90	88.86	88.86	*88.86*	
				Li-picrate					
t = 0°	λ_v =	31.7	32.4	33.1	33.4	33.6	—	*34.2*	*34.3*
	λ'_∞ =	33.9	34.0	34.1	34.1	34.1	—	*34.1*	
				K-picrate					
t = 0°	λ_v =	51.9	52.9	53.9	54.4	54.7	55.0	*55.5*	—
	λ'_∞ =	55.49	55.50	55.58	55.58	55.55	55.44	*55.5*	—

Tetrapropylammonium iodide, $N(C_3H_7)_4I$, (Bencowitz and Renshaw),[1] $t = 25°$

$c \times 10^3 =$	0.6477	0.54247	0.49952	0.11025
$\lambda_{found} =$	98.113	98.282	98.352	98.266
$\lambda_{\infty\,calc} =$	99.85	99.87	99.95	99.99
$c \times 10^3 =$	0.060061	0.05112		
$\lambda_{found} =$	99.460	99.482	99.69	and 100.1
$\lambda_{\infty\,calc} =$	99.99	99.98	100.0	

From the $1/\lambda_c,\kappa$-curve (κ = specific conductivity) Bencowitz and Renshaw find $\lambda_\infty = 99.69$. Using the square-root formula (or the $\lambda_c,\sqrt{c}$-curve) λ_∞ is found to equal 100.1. The value calculated by Walden, $\lambda_\infty = 100.0$, can be regarded as identical with the second of the two found by Bencowitz and Renshaw.

The limiting values λ'_∞ in Table XVII were first determined[2] in accordance with the latter formula and then subsequently by the square-root formula (II).

These observations of Table XVII also fall in line with the simpler formula (b) and consequently bring out the similarity in behavior of the so-called typical, strong binary salts. The results of Bencowitz and Renshaw involve salts with complex cations; those given above, salts containing complex anions, such as the picrate ion. In both cases, however, they act in practically the same manner. The alkylated sulphonium and ammonium salts give the most consistent calculated λ_∞ values for even the highest dilutions ($v = 100000$). Walden's investigations show that the formula may be valid to a minimum dilution $v \geq 100$. This same formula has been used to calculate the degree of dissociation α:[3]

$$\alpha = \frac{\lambda_v}{\lambda_\infty} = \frac{v^{0.5}}{v^{0.5} + 0.692}$$

II. CALCULATION OF λ_∞ IN METHYL ALCOHOL

Let us next investigate methyl alcohol as a solvent. One may ask: Do analogous relationships hold for the

[1] J. Am. Chem. Soc., 48, 2154 (1926).
[2] Walden, Z. physik. Chem., 108, 341 (1924).
[3] See page 170.

TABLE XVIII

KBr (Frazer and Hartley)

$c \times 10^4$ =	1.4643	10.633	5.0406	7.9683	0.8058	15.094	0
λ_{found} =	106.14	100.83	103.48	101.98	106.99	99.25	*109.35*
$\lambda_{\infty\ calc.}$ =	109.48	109.41	109.55	109.48	109.48	109.31	109.48

NaCl (Frazer and Hartley)

$c \times 10^4$ =	1.1232	6.9760	9.835	0
λ_{found} =	94.44	90.80	87.94	*96.95*
$\lambda_{\infty\ calc.}$ =	97.05	97.05	97.08	97.06

CsCl (Frazer and Hartley)

$c \times 10^4$ =	1.3395	1.6235	3.5656	5.6307	0
λ_{found} =	110.00	109.90	108.10	106.61	*113.60*
$\lambda_{\infty\ calc.}$ =	113.30	113.56	113.43	113.21	113.4

RbCl (Frazer and Hartley)

$c \times 10^4$ =	2.1191	3.8715	0
λ_{found} =	104.57	103.11	*108.65*
$\lambda_{\infty\ calc.}$ =	108.55	108.34	108.5

LiCl (Frazer and Hartley)

$c \times 10^4$ =	2.0873	6.6060	9.1401	0
λ_{found} =	87.60	85.19	84.15	*90.91*
$\lambda_{\infty\ calc.}$ =	90.90	90.90	90.90	90.90

$N(C_2H_5)_4$ picrate (Walden, Ulich and Busch)

v =	1000	2000	5000	10000	∞
λ_{found} =	96.1	98.1	99.8	1007	*102.9*
$\lambda_{\infty\ calc.}$ =	104.4	103.0	103.5	103.3	103.0

$LiNO_3$ (Frazer and Hartley)

$c \times 10^4$ =	1.7422	1.5988	3.2451	5.5701	7.5545	0
λ_{found} =	96.89	96.96	95.62	94.34	93.44	*100.25*
$\lambda_{\infty\ calc.}$ =	100.23	100.16	100.12	100.14	100.14	100.16

NaI (Dutoit), t = 18°,

v =	1000	2000	5000	10000	∞
λ_{found} =	84.6	86.4	88.0	88.9	(*91.2*)
$\lambda_{\infty\ calc.}$ =	91.16	91.44	91.25	91.22	91.26

LiBr (Völlmer), t = 18°

v =	1174	3717	11.740	∞
λ_{found} =	69.8	72.4	73.4	(*74.9*)
$\lambda_{\infty\ calc.}$ =	75.13	75.4	75.17	75.2

$N(C_2H_5)_4I$ (Walden), t = 25°

v =	800	1600	∞
λ_{found} =	107.5	110.4	*118*
$\lambda_{\infty\ calc.}$ =	117.42	117.60	117.6

$N(C_5H_{11})_4I$ (Walden), t = 25°,

λ_{found} =	78.9	80.6	*86*
$\lambda_{\infty\ calc.}$ =	86.17	85.86	86

Table XIX

Calculation of the Degree of Dissociation $\alpha_I = \lambda_v/\lambda_\infty$ *in methyl alcohol by the formula:*

$$\alpha_{II\ calc.} = \frac{v^{0.5}}{v^{0.5} + 2.61}$$

LiCl

$\lambda_\infty = 90.90$

$c \times 10^4 = 2.0873$ ($v = 4791$)		6.606 ($v = 1514$)
$\alpha_I = \frac{87.60}{90.90} = 0.9637$		$\alpha_I = \frac{85.19}{90.90} = 0.09372$
$\alpha_{II\ calc.} = 0.9636$		$\alpha_{II\ calc.} = 0.9371$

KBr

$\lambda_\infty = 109.35$

$c \times 10^4 = 15.094$ ($v = 662.5$)		0.8058 ($v = 12410$)
$\alpha_I = \frac{\lambda_v}{\lambda_\infty} = \frac{99.25}{109.35} = 0.9077$		$\alpha_I = \frac{106.99}{109.35} = 0.978$
$\alpha_{II\ calc.} = 0.9079$		$\alpha_{II\ calc.} = 0.977$

KCl

$\lambda_\infty = 105.05$

$c \times 10^4 = 1.5917$ ($v = 6287$)	$c = 4.0912$, $v = 2444$	$c = 1.0951$, $v = 9132$
$\alpha_I = \frac{101.80}{\lambda_\infty} = 0.969$	$\alpha_I = \frac{99.76}{105.05} = 0.9496$	$\alpha_I = \frac{102.25}{105.05} = 0.973$
$\alpha_{II\ calc.} = 0.968$	$\alpha_{II\ calc.} = 0.9498$	$\alpha_{II\ calc.} = 0.974$

$LiNO_3$

$\lambda_\infty = 100.25$

$c \times 10^4 = 7.5545$, $v = 1324$	$c = 3.2451$, $v = 3082$,	$c = 1.7422$, $v = 5740$
$\alpha_I = \frac{\lambda_v}{\lambda_\infty} = \frac{93.44}{100.25} = 0.9322$	$\alpha_I = \frac{95.62}{100.25} = 0.9538$	$\alpha_I = \frac{96.89}{100.25} = 0.9665$
$\alpha_{II\ calc.} = 0.9329$	$\alpha_{II\ calc.} = 0.9549$	$\alpha_{II\ calc.} = 0.9667$

Conductivity values λ_v and λ_∞ are those given by Frazer and Hartley (1925).

strong binary salts in methyl alcoholic solution? Let us examine the following empirical equation for the limiting value,

$$\lambda_\infty \text{ calc.} = \lambda_v (1 + 2.61/v^{0.5})$$

Table XVIII shows that the maximal conductivities λ_∞ for typical binary salts, as calculated by the empirical equation given above, are in fair agreement with those in italics which were obtained experimentally by extrapolation in accordance with the square-root formula. The same equation can be transformed and used to calculate the degree of dissociation at any dilution, v, using but one constant (K = 2.61), viz.:

$$\alpha = \frac{\lambda_v}{\lambda_\infty} = \frac{1}{1 + 2.61/v^{0.5}} = \frac{v^{0.5}}{v^{0.5} + 2.61}$$

If the above simple relation between the degree of dissociation, $\alpha = \lambda_v/\lambda_\infty$, and the dilution, v, holds for the typical binary salts (*i. e.* alkali halides and lithium nitrate) from v = 1000 liters upward, and represents the uniformity of the dissociation process for this class of salts, then it is possible to represent the latter by a uniform numerical expression for the dissociation as the v-values increase. This has been attempted in Table XX at

$$t = 25° \text{ and } \alpha = \frac{v^{0.5}}{v^{0.5} + 2.61}.$$

TABLE XX

Calculation of the "Degree of Dissociation", α, for Uni-univalent Salts (Alkali Halides) in Methyl Alcohol

t = 25°	v = 500	1000	2000
$\alpha_{calc.}$	= 0.8955	0.9244	0.9449
α_{Gosh}*	= ——	0.913	0.930
t = 25°	v = 5000	10000	12000
$\alpha_{calc.}$	= 0.9644	0.9746	0.9767
α_{Gosh}*	= 0.948	0.959	——

* See Partington, J. Chem. Soc., 99, 1937 (1911); Arrhenius, Z. physik. Chem., 100, 22 (1922).

Table XXI gives further observational data on the conductivity, λ_v, of binary salts, chiefly of the *ammonium type*. The limiting conductivity, λ_∞, has been extra-

TABLE XXI

Conductivities in Methyl Alcohol as Solvent. t = 25°

v = 100	500	1000	2000	∞
	1. NaBr (Goldschmidt)			
λ_v = 80.3	90.9	94.1	96.7	101.5
α = 0.791	0.896	0.927	0.953	1.00
	2. $NaOC_6H_2(NO_2)_3$ (Goldschmidt)			
λ_v = 71.0	82.8	86.6	89.8	95
α = 0.747	0.872	0.912	0.945	1.00
	3. $N(CH_3)_4I$ (Walden 1913)			
λ_v = 95.9	111.8	115.9	119.3	126
α = 0.761	0.887	0.920	0.947	1.00
	4. $N(C_2H_5)_4I$ (Walden 1913)			
λ_v = 91.4	104.3	108.2	111.0	118
α = 0.775	0.884	0.917	0.941	1.00
	5. $N(C_2H_5)_4$-picrate (Walden, Ulich and Laun)			
λ_v = 81.3	93.3	96.1	98.1	102.9
α = 0.790	0.907	0.934	0.953	1.00
$\alpha_{aver.}$ =	0.892	0.922	0.947	
	$N(CH_3)_4Cl$ (Walden, Ulich and Laun)			
λ_v = 90.8	103.5	107.4	109.6	117
α = 0.776	0.885	0.918	0.937	1.00
	$(C_4H_9)NH_3Cl$ (Walden, Ulich and Laun)			
λ_v = 77.6	86.7	89.9	92.4	98.8
α = 0.785	0.878	0.910	0.935	1.00
	$(C_2H_5)_2NH_2Cl$ (Walden, Ulich and Laun)			
λ_v =	93.4	97.3	100.5	108.3
α =	0.862	0.898	0.928	1.00

polated in every case in accordance with the *square-root law*. The corresponding degrees of dissociation values, $\alpha = \lambda_v/\lambda_\infty$ have also been included.

Table XXII

Ethyl Alcohol as solvent, Dielectric Constant $\epsilon_{25°} = 24$. *(Observed degree of dissociation* $\alpha = \lambda_v/\lambda_\infty$*).* $t = 25°$

Typical Binary Salts (alkali and quaternary ammonium salts)

	v =	100	200	500	1000	∞	
Potassium iodide KI	λ_v =	33.54	37.24	41.2	43.2	50.9	Walden
	α =	0.659	—	0.809	0.849		
Sodium chloride NaCl	λ_v =	—	—	33.7	36.2	43.5	Goldschmidt
	α =	—	—	0.775	0.832		
Lithium chloride LiCl	λ_v =	25.1	(28.0)	30.9	33.5	39	Goldschmidt
	α =	0.644	—	0.792	0.859		
Ammonium chloride NH_4Cl	λ_v =	26.84	—	34.9	37.47	45.3	Goldschmidt
	α =	0.593	—	0.770	0.827		
Silver nitrate $AgNO_3$	λ_v =	22.16	—	—	34.95	—	Getman
Tetraethylammonium iodide $N(C_2H_5)_4I$	λ_v =	31.7	(36.3)	42.1	—	53	Philip
	α =	0.598	—	0.794	—		
	λ_v =	31.87	—	42.9	46.4	55	Walden
	α =	0.580	—	0.780	0.844		
Tetramethylammonium chloride $N(CH_3)_4Cl$	λ_v =	29.2	—	38.6	41.9	50.6	Walden, Ulich and Laun
	α =	0.577	—	0.763	0.828		
Tetraethylammonium picrate, $N(C_2H_5)_4.OC_6H_2(NO_2)_3$	λ_v =	32.35	—	41.1	43.85	51.5	Walden, Ulich and Laun
	α =	0.628	—	0.798	0.851		

(Table XXII continued on page 226)

TABLE XXII (continued)

Salts of primary, secondary and ternary amine bases

	v = 100	200	500	1000	∞	
Ethylammonium bromide $(C_2H_5)NH_3Br$	$\lambda_v = 29$ (v = 20, λ = 20.1; v = 50, λ = 24.5)					Walden (1913)
Isobutylammonium chloride $(C_4H_9)NH_3Cl$	$\lambda_v = 25.1$	—	33.0	35.6	42.3	Walden, Ulich and Laun
	$\alpha = 0.593$	—	0.780	0.842		
Aniline hydrochloride $C_6H_5NH_2 \cdot HCl$	$\lambda_v = 23.6$	27.6	31.8	34.8	(44)	Walden (1913)
	$\alpha = 0.536$	—	0.723	0.791		
Aniline picrate $(C_6H_5)NH_2.HOC_6H_2(NO_2)_3$	$\lambda_v = 24.5$	28.3	32.9	36.1	(45)	Walden (1913)
	$\alpha = 0.544$	—	0.731	0.800		
Diethylammonium chloride $(C_2H_5)_2NH_2Cl$	$\lambda_v = 25.2$	30.0	35.4	38.8	47.1	Walden, Ulich and Laun
	$\alpha = 0.535$	—	0.752	0.824		
Piperidine picrate $(C_5H_{10})NH \cdot HOC_6H_2(NO_2)_3$	$\lambda_v = 25.2$	29.96	35.3	38.9	49	Walden (1913)
	$\alpha = 0.515$	—	0.720	0.792		
Tri-isoamylammonium picrate $(C_5H_{11})_3N \cdot HOC_6H_2(NO_2)_3$	$\lambda_v = 19.84$	24.15	29.15	32.44	41	Walden (1913)
	$\alpha = 0.484$	—	0.711	0.791		
Piperidine chloride $(C_5H_{10})NH_2Cl$	$\lambda_v = 24.4$	28.9	34.7	38.6	48.5	Goldschmidt
	$\alpha = 0.503$	—	0.615	0.796		

In general it may be said (1) that the conductivities of the mono-, di-, and tetra-substituted ammonium salts are of the same order of magnitude, (2) that the observed "degree of dissociation" values (for v = 500–2000) for salts 1 to 5 agree with the calculated ones (Table XX), and (3) that only inconsiderable differences are apparent in the degree of dissociation values of the mono-, di- and tetra-alkylated ammonium chlorides. The behavior of these salts in methyl alcoholic solution is therefore analogous to that in aqueous solution.

III. SOLUTIONS IN ETHYL ALCOHOL

As an examination of our Table XXII will readily show, our binary salts include the most diverse cations and the strongest anions. The table shows, furthermore, that the λ_v-values from v = 100 and upwards are of the same order of magnitude for all salts. Since the maximal conductivities for the various salts lie between 40 and 50, the degree of dissociation values, $\alpha = \lambda_v/\lambda_\infty$, also do not show considerable differences at corresponding dilutions. Of particular interest for our subsequent considerations, is the behavior of the *alkylated ammonium chlorides*. As indicated in Table XXIII there is no sharply decided difference in the degree of dissociation of these mono-, di-, or tetra-alkylated ammonium chlorides, especially at dilutions v ≷ 500.

TABLE XXIII

Degree of Dissociation of Alkylated Ammonium Salts in Ethyl Alcohol

	$(C_4H_9)NH_2.HCl$	$(C_2H_5)_2NH.HCl$	$(CH_3)_4NCl$	LiCl	NH_4Cl
v = 100, α =	0.593	0.535	0.577	0.644	0.593
v = 500, α =	0.780	0.752	0.763	0.79	0.770
v = 1000, α =	0.842	0.824	0.824	0.859	0.827

It should be emphasized that the two simple salts, lithium chloride and ammonium chloride also behave in the normal fashion, that is, dissociate like sodium chloride.

Table XXIV gives the degree of dissociation values at high dilutions.

TABLE XXIV

Degree of Dissociation Values of Various Salts in Ethyl Alcohol at High Dilutions

$t = 25^\circ$	$v = 2000$	5000	10000	∞	
$N(C_2H_5)_4I$	$\lambda = 49.0$	—	—	55	Walden
	$\alpha = 0.891$	—	—		
$N(C_2H_5)_4$-picrate	$\lambda = 45.95$	47.90	48.97	51.5	Walden, Ulich and Laun
	$\alpha = 0.892$	0.930	0.951		
$N(CH_3)_4Cl$	$\lambda = 44.5$	46.7	—	50.6	Walden, Ulich and Laun
	$\alpha = 0.880$	0.923	—		
NaCl	$\lambda = 38.26$	40.32	—	43.3	Goldschmidt
	$\alpha = 0.884$	0.931	—		
$N(C_4H_9)H_3Cl$	$\lambda = 37.6$	39.3	—	42.3	Walden, Ulich and Laun
	$\alpha = 0.889$	0.929	—		
Average value	$\alpha = 0.887$	0.928	0.951		

TABLE XXV

Calculation of Maximal Conductivity λ_∞ in Ethyl Alcohol

$$\lambda_\infty = \lambda_v (1 + 5.64/v^{0.5}).\ t = 25^\circ$$

	$v = 1000$	2000	5000	100000	∞	
$N(C_2H_5)_4$-picrate	$\lambda_v = 43.85$	45.95	47.90	48.97	*51.5*	
	$\lambda_{\infty\,calc} = 51.7$	51.7	51.7	51.7	51.7	
$N(CH_3)_4Cl$	$\lambda_v = 41.9$	44.4	46.7	—	*50.6*	
	$\lambda_{\infty\,calc} = (49.4)$	50.2	50.4	—	50.4	
$N(C_2H_5)_4I$	$\lambda_v = —$	49.0	—	—	*55*	
	$\lambda_{\infty\,calc} = —$	55.1	—	—	55.1	
$N(C_4H_9)H_3 \cdot Cl$	$\lambda_v = 35.6$	37.6	39.3	—	*42.3*	
	$\lambda_{\infty\,calc} = 42.0$	42.35	42.44	—	42.3	
	$v = 1230$	2460	4920	∞		
NaCl	$\lambda_v = 37.16$	38.72	40.26	*(43.3)*	Gold-	
	$\lambda_{\infty\,calc} = 43.14$	43.12	43.49	43.3	schmidt	
	$v = 512$	1024	2048	∞		
KI	$\lambda_v = 41.30$	43.49	45.44	*50.9*	Walden	
	$\lambda_{\infty\,calc} = (51.6)$	51.1	51.1	51.1		

For strong binary (uni-univalent) salts the above equation, containing the constant $K = 5.64$, yields λ_∞-values which are in fair agreement with those obtained by extra-

polation (italics) using the square-root formula. The same equation may be employed, then, for the direct calculation of the degree of dissociation $\alpha = \lambda_v/\lambda_\infty$.

$$\alpha_{calc.} = \frac{v^{0.5}}{v^{0.5} + 5.64}$$

	v =	500	1000	2000	5000	10000	20000
α_{calc}	=	0.796	0.849	0.888	0.926	0.947	0.962
$\alpha_{obs.\ mean}$	=		0.827 0.859	0.887	0.928	(0.951)	

IV. BINARY SALTS IN ACETONE SOLUTIONS

Proof of the dv-*formula (Ostwald-Walden-Bredig rule) in Acetone.*

In accordance with the empirical formula

$$_\infty - \lambda_v = dv = \frac{K}{\epsilon \cdot \eta \cdot v^{0.5}}$$

set up by Walden[1] the equations

(1) $$dv = \frac{65.7}{21.2 \times 0.003158 \times v^{0.5}} = \frac{982}{v^{0.5}}$$

and

(2) $$\lambda_\infty = \lambda_v + dv,$$

may be applied to acetone solutions at 25°, where ϵ = dielectric constant = 21.2, η = viscosity = 0.003158, and K = universal constant = 65.7. The factor a in the Kohlrausch square root formula, $\lambda_\infty - \lambda_v = a/v^{0.5}$, has been replaced here by $a = K/\epsilon\cdot\eta = 982$. Let us test this formula with reference to its application to several strong binary salts. (Table XXVI).

The maximal conductivities λ_∞ given in italics in the λ_v-columns of Table XXVI were extrapolated by application of the square-root formula. They are practically identical with those calculated from the dv-formula.

[1] Z. anorg. Chem., **115**, 81 (1921).

TABLE XXVI

Proof of the dv *Formula in Acetone*[1]

$$\text{Calculated } (\lambda_\infty - \lambda_v) = \frac{65.7}{21.2 \times 0.003158 \times v^{0.5}} = \frac{982}{v^{0.5}}$$

v = 1/c	dv	λ_v found	$\lambda_\infty = \lambda_v + dv$	λ_v found	$\lambda_\infty = \lambda_v + dv$	calc. λ_v (185.6 − dv)	Δ
	Tetra-ethylammonium picrate				Potassium iodide		
2000	21.9	155.9	177.8	163.8	185.7	163.7	+0.1
5000	13.9	163.8	177.7	171.8	185.7	171.7	+0.1
10000	9.8	167.8	177.6	175.8	185.6	175.8	±0
20000	6.9	170.6	175.5	178.7	185.6	178.7	±0
50000	4.4	173.0	177.5	181.2	185.6	181.2	±0
100000	3.1	174.3	177.4	182.5	185.6	182.5	±0
∞	0.0	*177.3*	av. 177.5	*185.6*	av. 185.6		
	Dinitrophenylpyridinium picrate				Tetramethylammonium picrate		
2000	21.9	129.6	151.5	164.3	186.2		
5000	13.9	137.6	151.5	172.6	186.5		
10000	9.8	141.7	151.5	176.8	186.6		
20000	6.9	144.6	151.5	179.8	186.7		
50000	4.4	147.1	151.5	182.4	186.8		
100000	3.1	148.4	151.5	183.8	186.9		
∞	0.0	*151.5*	av. 151.5	*187.0*	av. 186.6		

[1] See Walden, Ulich and Busch, Z. physik. Chem., **123**, 457 (1926).

Another empirical formula for the calculation of the limiting conductivity, λ_∞, of strong binary (uni-univalent) salts in acetone is the following:

$$\lambda_\infty = \lambda_v \left(1 + \frac{5.65}{v^{0.5}}\right)$$

Results obtained with it are presented in Table XXVII.

TABLE XXVII

Limiting Conductivities λ_∞ in Acetone by the Formula $\lambda_\infty = \lambda_v (1 + 5.65/v^{0.5})$

Salts	v =	500	10000	20000	50000	100000	
KI	λ_v =	171.8	175.8	178.8	181.2	182.5	*185.6*
	$\lambda_{\infty(calc.)}$ =	185.5	185.7	185.8	185.8	185.75	185.7
NaI	λ =	170.7	174.8*	177.7	180.2	181.5	*184.6*
	$\lambda_{\infty(calc.)}$ =	184.3	184.7	184.8	184.7	184.7	184.64
$N(C_2H_5)_4ClO_4$							
	λ =	192.3	197.1	200.5	203.5	204.9	*208.7*
	$\lambda_{\infty(calc.)}$ =	207.7	208.2	208.5	208.6	208.6	208.6
$N(C_2H_5)_4$-picrate	λ =	163.8	167.8	170.6	173.0	174.3	*177.3*
	$\lambda_{\infty(calc.)}$ =	177.0	177.3	177.4	177.4	177.4	177.4
$N(CH_3)_4$-picrate	λ =		176.8	179.8	182.4	183.8	*187.0*
	$\lambda_{\infty(calc.)}$ =		186.8	187.0	187.0	187.1	187.0
$N(C_3H_7)_4$-picrate	λ =	146.3	149.3	151.4	153.3	154.3	*156.6*
	$\lambda_{\infty(calc.)}$ =	158.0	157.7	157.4	157.2	157.1	157.3
$N(C_2H_5)_4I$	λ =		195.6	199.6	203.0	204.8	*(209)*
	$\lambda_{\infty(calc.)}$ =		206.6	207.6	208.1	208.5	(208.5)

For uni-bivalent salts $\lambda_\infty = \lambda_v \left(1 + \frac{n_1 \times n_2 \times 5.65}{v^{0.5}}\right) = \lambda_v \left(1 + \frac{11.30}{v^{0.5}}\right)$

½ $Ba(ClO_4)_2$ λ =		185.2	189.9	194.0	196.2	(201.2)
$\lambda_{\infty(calc.)}$ =		206.1	205.0	203.8	203.2	(203)

*McBain and Coleman (cf. Trans. Faraday Soc. 1919) found λ_v = 173.6 for NaI in acetone at 25° and at a dilution, v = 10000.

Comparison of the calculated maximal values—from figures covering a dilution range v = 5000 to 100000—with

TABLE XXVIII

Degree of Dissociation $\alpha = \lambda_v/\lambda_\infty$ *of the Typical Strong Binary Salts in Acetone.* $t = 25°$

v	KI		NaI		$N(C_2H_5)_4ClO_4$		$N(C_2H_5)_4$-picrate		$N(CH_3)_4$-picrate		Average
	λ	α	λ	α	λ	α	λ	α	λ	α	α_m
∞	185.6	1.000	184.6	1.000	208.7	1.000	177.3	1.000	187.0	1.000	1.000
100 000	182.5	0.983	181.5	0.983	204.9	0.982	174.3	0.983	183.8	0.983	0.9828
50 000	181.2	.976	180.2	.976	203.5	.975	173.0	.976	182.4	.975	0.9756
20 000	178.7	.963	177.7	.963	200.5	.961	170.6	.962	179.8	.962	0.9622
10 000	175.8	.947	174.8	.947	197.1	.944	167.8	.946	176.8	.945	0.9458
5 000	171.8	.926	170.7	.925	192.3	.921	163.8	.924	172.6	.923	0.924
2 000	163.8	.883	162.8	.882	182.9	.876	155.9	.879	164.3	.879	(0.880)
1 000	155.2	.836	155.1	.840	173.4	.831	148.1	.835	155.9	.834	(0.835)

those extrapolated in accordance with the square-root formula again shows excellent agreement. This same equation can be altered and used for the calculation of the degree of dissociation $\alpha = \lambda_v/\lambda_\infty$. In Table XXVIII are given the α values as obtained from experimental data.

Let us compare the average α values given in Table XXVIII above with those calculated on the basis of the equation

$$\alpha = \frac{v^{0.5}}{v^{0.5} + 5.65}$$

v =	1000	2000	5000	10000
$\alpha_{calc.}$ =	0.8485	0.8879	0.9260	0.9465
α_m =	0.835	0.880	0.924	0.9458
		(0.883-0.876)	(0.926-0.921)	(0.947-0.944)

v =	20000	50000	100000
$\alpha_{calc.}$ =	0.9616	0.9754	0.9824
α_m =	0.9622	0.9756	0.9828
	(0.963-0.961)	(0.976-0.975)	(0.983-0.982)

From these figures it is evident that the classic degree of dissociation (conductivity coefficient) $\alpha = \lambda_v/\lambda_\infty$ of all these salts is practically identical beginning at dilutions $v \geqq 5000$. This group includes sodium and potassium iodides and the tetra-alkylated[1] ammonium perchlorates and picrates. The α-values for this class of "similarly dissociated" strong salts can be readily calculated in advance and with satisfactory accuracy, by means of the above equation.

SUMMARY

The validity of Kohlrausch's square-root formula $\lambda_\infty = \lambda_v + a\sqrt{c}$ for the extrapolation of the maximal conductivity λ_∞ in many different solvents was demonstrated in Chapter II. Moreover, several empirical formulas for computing this limiting value were subsequently tested and their limits of applicability to strong binary salts determined.

[1] The behavior of mono- and di-alkylated ammonium salts will be discussed later.

By means of the tabulated values of λ_v and λ_∞ the "degree of dissociation" $\alpha = \lambda_v/\lambda_\infty$ for a series of salts in methyl and ethyl alcoholic solutions, as well as in acetone, were next worked out. These α-values for various "strong" salts were found to be practically the same at equivalent dilutions in each solvent. Empirical rules for the calculation of these average values were presented.

These calculated α-values $= \frac{v^{0.5}}{v^{0.5} + K}$ which were found to agree with the mean values of $\alpha = \lambda_v/\lambda_\infty$ for typical strong binary salts, may be used yet further. One may ask: Upon which of the characteristic physical properties of an ionizing solvent is the "degree of dissociation" $\alpha = \lambda_v/\lambda_\infty$ dependent? The answer is: Upon the dielectric constant ϵ. The following examples demonstrate this relationship in a general manner and aim to establish a numerical relationship between similar α values, in various media at the corresponding dilutions v, and the dielectric constant ϵ of the pure solvent.

Thus,

where $\alpha = 0.976 - 0.970 =$ constant:

solvent:	ϵ	v	$\epsilon\sqrt[3]{v} \sim$ const.	
water	80	800	743	average 750
methyl alcohol	32	12000	733	
acetone	21	50000	774	

when $\alpha = 0.924 =$ constant:

water	80	68	327	average 330
methyl alcohol	32	1000	320	
acetone	21	4500	347	

when $\alpha = 0.88 - 0.89 =$ constant

water	80	30	249	average 260
methyl alcohol	32	500	255	
ethyl alcohol	24	1400	269	
acetone	21	2000	265	

Approximately equal values of the degree of dissociation $\alpha = \lambda_v/\lambda_\infty$ for typical binary salts in various solvents obtain when

$$\epsilon_1\sqrt[3]{v_1} = \epsilon_2\sqrt[3]{v_2} = \text{constant.}$$

This relationship was established empirically[1] as early as 1905 to bring out the fact that the "degree of dissociation", α, is dependent upon the dielectric constant ϵ of the ionizing solvent under consideration. It is apparent that enormous differences in dilution, *e. g.* water and acetone, often characterize comparable conditions of electrolytes when α-values are the same. Sementschenko recently pointed out an interesting deduction from this relationship.[2]

If we compare the values of the "non-dissociated" part $(1 - \alpha)$ with the numerical values of the product we find the following approximate relationship:

I	$\alpha_1 = 0.976$	$(1 - \alpha_1) = 0.030$
	$- 0.970$	
II	$\alpha_2 = 0.924$	$(1 - \alpha_2) = 0.076$
III	$\alpha_3 = 0.89$	$(1 - \alpha_3) = 0.110$

I	$\epsilon\sqrt[3]{v} = 750$	$(1 - \alpha_1)\epsilon\sqrt[3]{v} = 22.5$	average 25.5
II	" $= 330$	$(1 - \alpha_2)\epsilon\sqrt[3]{v} = 25.0$	
III	" $= 260$	$(1 - \alpha_3)\epsilon\sqrt[3]{v} = 28.6$	

At first glance it would seem that the curious relationship $(1 - \alpha)\epsilon\sqrt[3]{v} \sim 25.5 \sim$ constant, were applicable here. We must remember that this relation is built on the following facts: (1) Dilutions $v = 30$ to 50000 in totally different solvents, (2) dielectric constants from $\epsilon = 80$ to $\epsilon = 21$, (3) "degree of dissociation" $\alpha = \lambda_v/\lambda_\infty = 0.89$ to 0.970, and (4) different binary strong salts. In general, the comparative data and tables presented, including molecular conductivity λ_v and "degree of dissociation" $\alpha = \lambda_v/\lambda_\infty$ values, have demonstrated that the strong binary salts discussed above behave *similarly* at high dilutions when water, methyl alcohol, ethyl alcohol and acetone are employed as ionizing solvents.

[1] Walden, Z. physik. Chem., **54**, 228 (1905).
[2] Sementschenko, Z. physik. Chem., **112**, 128 (1924).

CHAPTER X

Do Typical Binary Salts which are Found to be Equally Strong in Equivalent Aqueous Solutions, Retain this same Relationship in Non-Aqueous Solutions?

In view of the contrast between alkali metal and halogen, it is generally assumed that heteropolar character is most sharply accentuated in uni-univalent salts of the type of sodium chloride. On the basis of the Lewis-Langmuir theory the halogen atom lacks but one electron in its outer shell to resemble the structure of the inert gases. Consequently, the halogen easily accepts another electron from its partner in a salt, the latter becoming the cation, the halogen the anion.

From the standpoint of the modern theory of dissociation are such typical binary salts weakly or strongly dissociated? Schreiner[1] believes "that most salts may be considered as completely dissociated even in non-aqueous solvents."

We have shown that λ,v-curves and the "degree" of dissociation values—as expressed by the relationship $\alpha = \lambda_v/\lambda_\infty$—for a certain group of typical binary salts are similar in aqueous, methyl and ethyl alcoholic solutions. These salts collectively have been characterized as *strong* electrolytes. We may justly ask whether this similarity in behavior is a characteristic of salts in all solvents, or whether the *chemical* nature of the latter exerts any influence? Further, is this tendency toward dissociation of a given simple salt type, MX, dependent upon that particular type, or does chemical structure enter as the principal determinant? This same question may be asked in a more concrete form: Are salts of the same type–such

[1] Z. physik. Chem., 111, 427 (1924).

as KI, NaI, LiCl, $N(R_4)Cl$, $N(R)_3HCl$, $N(R_2)H_2Cl$, $N(R)H_3Cl$[1]–which are dissociated to practically the same degree in water, ethyl alcohol and methyl alcohol, really similar electrolytes? We may go further and ask: Is the process of solution an essentially physico-mechanical phenomenon; or is the solution as well as the dissociation of even the simplest salt molecules due to the measureable co-operation of "chemical" factors or "individual moments" depending on the salt and the solvent?

Experimentally it had been ascertained that at high dilutions the properties of different electrolytes become less and less distinctive, in that the behavior of the various binary salts becomes more and more alike. Consequently, to answer the questions which have just been advanced, it was necessary first of all to subject the field of moderately *concentrated* solutions to experimental treatment. Non-aqueous and non-alcoholic solvents of different structure, as acetone, acetonitrile, nitrobenzene, sulphurous acid, and hydrocarbons, were employed. In particular were acetone solutions of salts and the hydrocarbons investigated. Experiments in the range of *high* dilutions were next carried out. Attempts were also made to determine experimentally the part played by the anion—the various halogen and complex organic ions, for example, picrate anion —in the case of the same or similarly conducting cations.

Table XXIX gives a summary of the results obtained by Walden (1911-1912) in acetone solutions. No great accuracy is claimed for the λ-values. They do, however, offer a means of comparison.

A casual survey of the values of λ_v in Table XXIX will readily convince one that the Acetone solutions of this great class of *similar*, *typical*, *binary ammonium salts* can be divided into a host of groups so far as behavior is concerned. Salts of the same type, which had given similar or practically identical conductivity values even in ethyl alcohol, seem to belong to altogether different classes,

[1] Where R = alkyl radical.

TABLE XXIX

Conductivity λ_v *in Acetone*, t = 25°

I. Tetra-alkylated ammonium salts $(R_4)NX$

	v = 100	200	400	500	800	1000	1600	3200	
$N(C_2H_5)_4Br$	—	115.0	134.8	—	153.1	—	168.8	180.6	(Walden 1912-13)
$N(C_2H_5)_4I$	113	128	—	151.3	—	166.8	—	184.1	(Walden 1905)
KI	112	128.8	144.6	147.8	157	169	—	—	(Walden 1905)
$N(C_5H_{11})_4I$	95.9	111.2	125	—	136.9	—	145.9	153	(Walden 1913)
$N(C_3H_7)_4I$	—	116.0	135.5	—	—	152.4	—	—	(Walden 1907)
$N(CH_3)_4SCN$	112.1	133.1	152.7	—	170.2	—	184.8	195.8	(Walden 1913)
LiBr	36.0	49.8	—	64.1	—	80.4	(95.7 at v = 2000)		(Sêrkov 1909)

Table XXIX—continued

II. Tri-alkylated ammonium salts $(R_3)HN{\cdot}X$

	v = 20	40	50	80	100	160	200	400	640	800
$(C_2H_5)_3HN{\cdot}Cl$	—	—	—	—	1.74	—	2.18	2.94	3.52	3.91
$(C_2H_5)_3HN{\cdot}Br$	—	—	—	4.62	5.00	—	6.62	9.0	11.20	—
$(C_2H_5)_3HN{\cdot}I$	20.0	25.6	—	33.0	35.4	—	45.5	57.8	68.7	—
$(C_3H_7)_3HN{\cdot}Cl$	1.55	1.72	—	2.03	2.16	2.53	—	—	—	—
$(C_3H_7)_3HN{\cdot}Br$	3.44	4.27	—	5.56	6.0	7.38	8.1	—	—	—
$(C_3H_7)_3HN{\cdot}F$	14.4	14.3 (!)	—	13.9 (!)	—	13.6 (!)	—	—	—	—
$(C_5H_{11})_3HN{\cdot}Cl$	1.37	1.53	—	1.81	—	—	—	—	—	—
$(C_5H_{11})_3HN{\cdot}Br$	2.81	3.46	—	4.51	4.89	6.07	6.65	—	—	—
$(C_5H_{11})_3HN{\cdot}F$	4.39	4.31	—	4.34	4.40	4.60	4.71	—	—	—
$(C_5H_{11})_3HN{\cdot}I$	—	22.46	—	28.98	31.3	38.19	41.2	—	—	—
$(C_5H_{11})_3HN{\cdot}SCN$	—	14.1	16.35	19.9	22.38	—	31.0	43.0	—	—
$(C_5H_{11})_3HN$-picrate	—	—	33.42	40.0	44.35	—	58.9	78.50	—	98.9
$C_6H_5(CH_3)_2HN{\cdot}Cl$	1.25	1.36	—	1.55	—	—	—	—	—	—
$C_6H_5(CH_3)_2HN{\cdot}Br$	1.61	1.89	2.03	2.36	2.59	—	3.44	—	—	—
$C_6H_5(CH_3)_2HN{\cdot}I$	12.8	16.5	17.6	20.8	22.1	26.1	27.7	—	—	—
LiCl	3.3	—	5.4	—	7.8	—	11.3	15.3 (Sêrkov)		

TABLE XXIX—continued

III. Di-alkylated ammonium salts $(R)_2H_2N{\cdot}X$.

	v = 20	40	50	80	100	160	200	400	640	800
$(C_2H_5)_2H_2N{\cdot}Cl$	—	—	—	—	3.79	—	4.71	5.84	—	6.20
$(C_2H_5)_2H_2N{\cdot}Br$	—	—	8.38	—	9.80	—	11.60	14.00	—	18.0
$(C_2H_5)_2H_2N{\cdot}I$	19.5	23.4	—	28.8	30.8	36.9	39.6	51.4	62.8	—
$(C_3H_7)_2H_2N{\cdot}Cl$	—	—	2.85	3.25	3.56	—	4.57	5.91	—	7.7
$(C_5H_{11})_2H_2N{\cdot}I$	15.72	19.7	21.1	25.2	27.1	32.8	35.3	46.0	55.7	—
$(C_5H_{11})_2H_2N{\cdot}SCN$	16.1	19.5	20.8	24.8	26.0	32.5	—	—	—	—
$(C_5H_{11})_2H_2N{\cdot}NO_3$	7.25	8.7	9.2	10.7	11.5	13.7	14.8	—	—	—
$(C_{11}H_9)_2H_2N{\cdot}F$	8.5	10.4	—	—	11.1	reverses at v=232	11.0!	9.3	—	—
$AgNO_3$	—	—	7.19	—	10.17	—	11.0	(12.54	v=500),	(14.62 v = 1000)

IV. Mono-alkylated (arylated) ammonium salts $RNH_3{\cdot}X$

	v = 20	40	50	80	100	160	200	400	640	800
$(C_2H_5)H_3N{\cdot}Br$	—	—	—	—	13.97	16.5	18.3	23.8	—	31.6
$(C_2H_5)H_3N{\cdot}I$	—	—	—	—	47.6	—	61.7	79.1	—	100.0
$(C_6H_5)H_3N$-picrate	—	—	36.5	72.4	46.0	52.3	56.7	68.4	—	—
Ammonium iodide NH_4I	—	—	—	—	60.0	—	76.4	95.2	—	116

as judged from the properties of their acetone solutions. Thus, where v = 200, we obtain the following λ_v-values for a number of such salts:

	$t = 25°$. $v = 200$. Ethyl alcohol	Acetone
Tetra-ethyl ammonium iodide, $N(C_2H_5)_4I$	= 36.3	128
Di-ethylammonium chloride, $N(C_2H_5)_2H_2Cl$	= 30.0	4.7
Lithium chloride, LiCl	= 28.0	11.3

If these be classified as in Table XXIX, that is, if they be grouped according to the degree of alkylation, and then, if each of these subdivisions be investigated with reference to the rôle played by the anion, the following conclusions may be drawn.

(a) On the basis of conductivity values, the tetra-alkylated ammonium halides are directly comparable with the typical binary salt potassium iodide.

(b) The halogenides of the tri-, di-, and mono-alkylated ammonium bases are more or less at variance with this group of strong binary salts. The following relationships, as measured by the λ_v-values, obtain among these three types of salts:

1. mono- > di- > tri-alkylated salts, in the case of the chlorides (and bromides).

2. mono- > tri- ≧ di-alkylated salts, in the case of the iodides.

(c) The influence of the anions, Cl^-, Br^-, I^-, is expressed in a very characteristic way in the conductivity values. Thus, at a dilution, v = 100, if for the iodide $\lambda = 100$, then

Cation		Anions I^-	Br^-	Cl^-
Triethyl—$N(C_2H_5)_3H^+$	λ_v =	100	14	5
Triamyl—$N(C_5H_{11})_3H^+$		100	14	6
Tripropyl—$N(C_3H_7)_3H^+$		—	14	5
Phenyldimethyl—$NC_6H_5(CH_3)_2H^+$		100	12.5	7.5
Diethyl—$N(C_2H_5)_2H_2^+$		100	32	12.5
Monoethyl—$N(C_2H_5)H_3^+$		100	32	—
Lithium—Li^+		100	36	7.8

In all three classes of compounds, namely, tri-, di-, and mono-substituted compounds, the iodides possess the

highest conductivity values, the chlorides the lowest. In the case of the tri-substituted ammonium salts the relation is such, that if the iodide has a λ-value of 100, that of the bromide will be 14 and that of the chloride, only about 6. As the number of substituents in the NH_4-radical decreases, the influence of the bromide ion jumps from 14 to 32—in the di- and mono-substituted ammonium bases. Apparently the anionic effect in the latter two groups of compounds is much like that in the lithium halides. The simply constituted electrolyte and typical binary salt lithium chloride, on the other hand, has conductivities analogous to the abnormal di- and tri-alkylated ammonium chlorides. The typical binary salt silver nitrate, resembles the abnormal di-alkylated ammonium nitrates in the same respect.

An attempt has been made to depict this varied behavior of the different alkylated ammonium salts in Fig. 9. For purposes of comparison, curves for several typical inorganic salts have also been drawn in. In considering these results the fact should be emphasized that the ion mobilities of the various alkylated cations on the one hand, and the halogen ions, on the other, are very close to each other at infinite dilution.

Let us review once more the facts in the case: On the basis of conductivity data that have long been known and repeatedly verified, it is generally assumed that the alkali halides—for instance, those of sodium, potassium, and lithium—are typical binary salts which are similar in behavior and dissociated to practically the same degree in water and alcohols. It has furthermore been assumed as true that salts made up of univalent radicals, such as the ammonium and alkylated ammonium bases, may be considered as typical binary salts which, like the alkali halides, "are dissociated to nearly equal extent in equivalent solutions."[1] Direct conductivity measurements in methyl and ethyl alcohol and water have verified this view.

However, in acetone solution conductivity measurements show that there has been a "separation" of these

[1] Nernst, *Theoretische Chemie*, 389, 417 (8th ed., 1921).

salts, previously considered similar and equally dissociated. They have divided into one group of "normal," strong or typical binary salts—the tetra-alkylated ammonium compounds—and several sub-groups of moderately

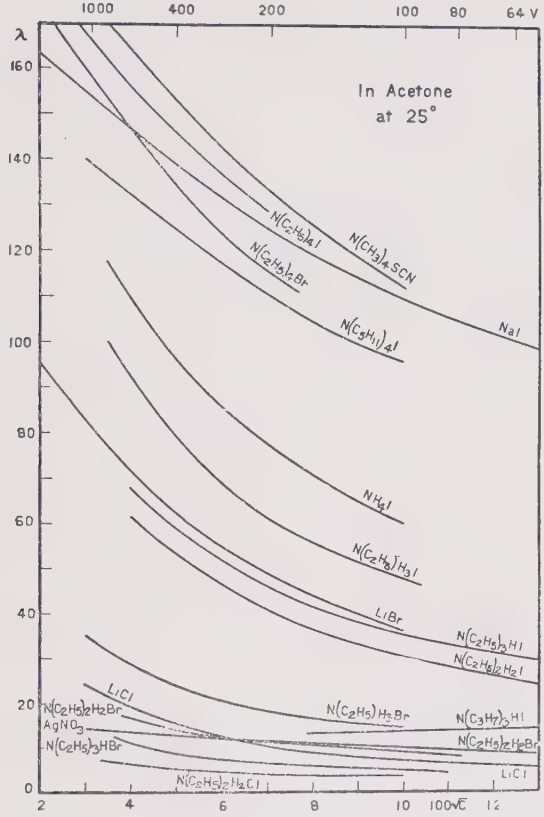


FIG. 9

strong to extremely weak, poorly conducting salts. These studies have revealed furthermore, that the conductivity values in each of these sub-groups shows a decided dependence on the nature of the halogen ion. This influence upon conductivity and upon "dissociation"—expressed by $\alpha = \lambda_v/\lambda_\infty$—can be illustrated by the following series.

Anions: picrate > iodide > thiocyanate > bromide > chloride. (The triamylamine salts of picric and thiocyanic acid have also been included).

It has definitely been shown that these extremely low conductivity values are not caused by solvolysis.[1] Experiments were carried out in which a current of dry air was passed through an acetone solution of the chloride and then into an aqueous solution of silver nitrate. No trace of a precipitate of AgCl was observed. Direct conductivity measurements, even at the very highest dilutions, have shown also that the poorly conducting salts in question possess normal ion mobilities. Later we shall learn that the ion mobilities, l, have the following values at 25°.

Ions:	$N(C_2H_5)_4^+$	$N(C_2H_5)_2H_2^+$	$N(C_4H_9)H_3^+$	Cl^-	I^-	Li^+
mobility	l = 93.0	91.1	92.1	105.1	116.0	70.6

Therefore, the extremely poor conductance of the chlorides, *e.g.* $N(C_2H_5)_2H_2 \cdot Cl$ and $N(C_4H_9)H_3 \cdot Cl$, can not be ascribed to the ion mobilities. The reason must be sought in the salts themselves, perhaps in their tendency towards ionization or in their constitution. It reminds one of the similar relationship met in the case of another class of electrolytes, namely, aqueous solutions of the acids. Organic acids in aqueous solution correspond to weak electrolytes. In solvents containing no hydroxyl, acids are practically non-electrolytes and the incompletely alkylated ammonium salts become "weak electrolytes."

The following classification and arrangement employs the conductivity as a measure of "strength":

Compounds	*Strong electrolytes*	*Weak electrolytes*
Tetra-alkylated ammonium halides and picrates $N(R)_4X$	In water $\epsilon = 80$, and other media (acetone, SO_2, $C_2H_4Cl_2$ etc.)	
Mono-, di- and tri-alkylated ammonium halides, lithium halides.	In water, in alcohols.	In acetone, $CHCl_3$ etc.

[1] This erroneous impression was held by Beutner, Z. Elektrochem., **25**, 98, 328 (1919). See also Thiel, *ibid.*, **25**, 214, 329 (1919).

Halogen hydracids, HX	In water, in alcohols	In acetone, $CHCl_3$ etc.
Organic carboxylic acids	(In sulphuric acid?)[1]	In water, alcohol, acetone, etc.

As early as 1912 Walden[2] separated the typical binary salts into weak and strong electrolytes, using as a criterion for this classification the varying influence of different alkylated ammonium salts upon the di-electric constant of the pure solvent. Although the tetra-alkylated ammonium salts are apparently to be counted among the strongest electrolytes, the halides of the mono-, di- and tri-alkylated ammonium bases, particularly the chlorides, are to be considered as a special class. These early findings were recently verified by our very precise measurements of the di-electric constants of solvents.[3] In particular did the measurements in acetone[4] show that the behavior of mono-, di-, and tri-alkylated ammonium chlorides was a peculiar one, and that these substances could hardly continue to be considered as typical electrolytes.

To bring out this difference in behavior in still another manner, the percentage "dissociation" $\alpha = \lambda_v/\lambda_\infty$ of these salts is given in Table XXX.

The salts noted in Table XXX dissociate in a similar manner in water, methyl alcohol and ethyl alcohol. The first five have practically identical α-values at similar dilutions in every one of these solvents. The data for acetone solutions indicate a division into two different classes; first, the strong salts $N(CH_3)_4Cl$ and $N(C_2H_5)_4I$ whose

[1] It is entirely possible that an ionizing medium exists which will dissociate the "weak" carboxylic acids to a high degree and change them into "strong" electrolytes. Such a medium must probably be of the type ROH with a di-electric constant higher than that of water. Perhaps pure sulphuric acid $SO_3H{\cdot}OH$ is such a solvent. From the investigations of Hantzsch, Z. physik. Chem., **61**, 296 (1908) and of Walden, Z. anorg. Chem., **29**, 383 (1902) one can conclude that acetic acid, benzoic acid, etc., form good conducting solutions in pure sulphuric acid and that the conductivity values are independent of the dilution, for example,

CH_3COOH, $\lambda = 64.5 - 65.0$,
C_6H_5COOH, $\lambda = 69.4 - 70.0$ (at 25°)

[2] Bull. acad. sci., St. Petersburg, 305, 330 (1912).

[3] Walden, Ulich and Werner, Z. physik. Chem., **116**, 268 (1925).

[4] Walden and Werner, *ibid.*, **124**, 412 (1926).

TABLE XXX

Degree of Dissociation in Various Solvents. $t = 25°$

Salts	Water		Methyl alcohol		Ethyl alcohol		Acetone	
	v	α	v	α	v	α	v	α
1. LiCl	100	0.925	100	0.80	100	0.64	100	0.044
	500	0.977	500	0.88	500	0.79	500	0.091
	1000	—	1000	0.91	1000	0.86	1000	—
2. $N(CH_3)_4.Cl$ (tetra-alkyl.)	100	0.920	100	0.78	100	0.58	100	—
	500	0.965	500	0.89	500	0.76	500	—
	1000	0.978	1000	0.92	1000	0.83	1000	0.77
3. $N(C_4H_9)H_3Cl$ (mono-alkyl.)	100	0.917	100	0.79	100	0.59	100	—
	500	0.959	500	0.88	500	0.78	500	0.061
	1000	0.975	1000	0.91	1000	0.84	1000	0.079
4. $N(C_2H_5)_2H_2Cl$ (di-alkyl.)	100	0.916	100	—	100	0.54	100	—
	500	0.961	500	0.86	500	0.75	500	0.061
	1000	0.975	1000	0.90	1000	0.82	1000	0.079
5. $N(C_2H_5)_4I$ (tetra-alkyl.)	100	0.933	100	0.78	100	0.60	100	0.54
	500	$t = 0°$	500	0.88	500	0.79	500	0.72
	1000		1000	0.92	1000	0.84	1000	0.79
Acetic acid CH_3COOH	100	0.042						
	500	0.086						
	1000	0.117						

degree of dissociation at a dilution of v = 1000, approximates α = 0.77 to 0.79, and secondly, the weak or slightly dissociated salts LiCl, $N(C_4H_9)H_3Cl$, $N(C_2H_5)_2H_2Cl$, whose α-value at the same dilution is $\leqslant$ 0.08. With reference to the degree of dissociation, the last mentioned salts in acetone solution are in much the same relationship to the tetra-alkylated salts as are the "weak" acids (*e.g.* acetic) to the "strong" or "moderately strong" acids in aqueous solution.

Thus far it has been the *cation* whose chemical nature has been reflected in the numerical size of the degree of dissociation. The influence of the *anion* also can be traced and Table XXXI gives some data on the conductivities of tetra-alkylated ammonium salts in acetone solutions. Let us first examine the *tetra-alkylated* salts as examples of strong binary electrolytes.

TABLE XXXI

Conductivities of Various Tetra-ethyl ammonium Salts in Acetone Solutions. t = 25°

Anion =	Picrate		Perchlorate		Iodide		Chloride	
v	λ_v	α	λ_v	α	λ_v	α	λ_v	α
1000	148.1	0.835	173.4	0.831	166.5	0.797	151.6	0.765
10000	167.8	0.946	197.1	0.944	195.6	0.936	182.6	0.922
20000	170.6	0.962	200.5	0.961	199.6	0.955	187.1	0.945
50000	173.0	0.976	203.5	0.975	203.0	0.973	191.2	0.965
∞	177.3	1.000	208.7	1.00	209.0	1.00	198.1	1.00

I. Arranged in order of the size of the α-values, the anionic influence employing *one and the same cation* at equal dilutions, is the following:

picrate ion $\geqq$ perchlorate ion > iodide ion > (bromide ion) > chloride ion.

This effect is noticeable even at such very great dilutions as v $\leqslant$ 20000, particularly when the two extremes (picrate and chloride) are compared. The difference between the iodide and chloride ions is also remarkable. It must be recalled that we have already met this specific factor in the discussion of measurements made at smaller dilutions, where its effect was even more pronounced.

II. It is interesting to note that the difference between the tetra-alkylated ammonium halides and the less alkylated compounds recurs in the case of the *picrates*. It is also noteworthy that an organic ion, such as the picrate ion, causes more pronounced dissociation than the typical halide ions did. However, the differences in α-values between the *tetra*-alkylated salts on the one hand and the mono- and di-alkylated derivates on the other are considerably increased. The λ- and α-values of several picrates are given in Table XXXII for comparison.

TABLE XXXII

Conductivity Data of Various Picrates. $t = 25°$

	$N(C_2H_5)_2H_2$-picrate		$N(C_4H_9)H_3$-picrate		Lithium picrate		$(N(C_2H_5)_4$-picrate	
v	λ_v	α	λ_v	α	λ_v	α	λ	α
1000	117.3	0.668	117.2	0.664	—	—	148.1	0.835
2000	133.3	0.759	133.4	0.755	116.4	0.751	—	—
5000	148.9	0.848	149.4	0.846	130.1	0.839	—	—
10000	156.7	0.892	157.3	0.891	137.4	0.887	167.8	0.946
20000	162.2	0.924	162.9	0.922	142.6	0.920	170.6	0.962
50000	167.1	0.952	168.0	0.951	147.1	0.949	173.0	0.976
∞	175.6	1.00	176.6	1.00	155.0	1.00	177.3	1.000

Several interesting points may be gleaned from the data presented in Table XXXII.

(1) The conductivity values, λ, of the mono- and di-alkylated ammonium salts are in general, lower than those of the tetra-alkylated ammonium picrates.

(2) The degree of dissociation values, $\alpha = \lambda_v/\lambda_\infty$, also are lower than those of the tetra-alkylated ammonium salts. However, they are of the same order of magnitude. The great numerical differences between their values, and those of the chlorides have disappeared.

(3) On the other hand the α-values become practically identical from $v \geqq 1000$ onward; that is, the picrates of lithium and of the mono- and di-alkylated ammonium bases are analogous electrolytes so far as the degree of dissociation is concerned. Lithium salts, therefore, are not directly comparable with the other alkali salts and the tetra-alkylated ammonium salts.

The differences and analogies, just mentioned are revealed in the dilution range, v = 1000 to 50000. They were already indicated during our consideration of more concentrated solutions. The conclusion had previously been drawn, from its low conductivity, that lithium chloride, resembled the hydrochlorides of the di- and tri-alkylated amines, and not the salts of the tetra-alkylated ammonium bases.

The chlorides of the mono- and di-alkylated amines form a new and distinctive sub-group. Table XXXIII summarizes the great differences in the λ_v- and $\alpha = \lambda_v/\lambda_\infty$-values between chlorides of the tetra-alkylated ammonium bases on the one hand, and those of the mono- and di-alkyl amines on the other.

For comparison let us take the values for the degree of dissociation α of these salts at high dilutions:

v =	1000	2000	3000	4000
$N(C_2H_5)_4Cl$	0.765	0.827	0.859	0.877
$N(C_2H_5)_2H_2Cl$	0.078	0.100	0.120	0.135
$N(C_4H_9)H_3Cl$	0.078	0.102	0.123	0.137

It is evident that even at the relatively high dilution v = 4000 the chlorides may be divided into *two* different classes. Judging from the percentage dissociation values it would seem logical to differentiate between strong and weak salts, much as strong and weak acids are considered in conjunction with the classical theory of dissociation. In furthering this analogy it would seem advisable to determine if the Ostwald dilution law is not also applicable here, as in the case of organic acids which are weak electrolytes.

Comparison of these three alkylated ammonium salts in the same dilution ranges v = 1000, 4000, 5000, reveals an unquestionable variance in K values. The two "weak" salts have a dissociation constant which does not diminish very much ($K = 5.8$ to 5.2×10^{-6} and $K = 6.2$ to 5.5×10^{-6}), whereas the K-values of tetra-ethylammonium picrate, a strong salt, are reduced by one half within the same dilution range ($K = 42.6$ to 22.1×10^{-4}) [See p. 251].

TABLE XXXIII

Contrasting λ- and α-values of the tetra- vs. the mono-alkylated Amines.

	$N(C_2H_5)_4Cl$		$N(C_2H_5)_2H_2Cl$		$N(C_4H_9)H_3Cl$	
v	λ	α	λ	α	λ	α
549	—	—	—	—	12.05	0.0610
660.5	—	—	12.36	0.0629	—	—
701.7	—	—	—	—	12.97	0.0657
792.4	—	—	13.28	0.0676	—	—
846	148.3	0.745	—	—	—	—
1000	151.6	0.765	—	0.078	—	—
1053	—	—	—	—	15.31	0.0776
1189	—	—	15.66	0.0797	—	—
1269	156.1	0.788	—	—	—	—
1762	—	—	—		19.14	0.0992
1990	—	—	19.66	0.100	—	—
2111	—	—	—		20.70	0.1049
2124	164.6	0.831	—			

	$N(C_2H_5)_4Cl$		$N(C_2H_5)_2H_2Cl$		$N(C_4H_9)H_3Cl$	
v	λ	α	λ	α	λ	α
2703	—	—	—	—	23.05	0.117
2988	169.9	0.858	—	—	—	—
3052	—	—	23.53	0.120	—	—
3586	172.2	0.869	—	—	—	—
3877	—	—	—	—	26.75	0.136
4000	—	0.877	—	0.135	—	0.137
4380	—	—	27.35	0.139	—	—
4585	175.4	0.885	—	—	—	—
∞	198.1	1.00	196.2	1.00	1.97.2	1.00

Lithium chloride

v = 100	200	400		∞
λ = 7.8	11.3	15.3		175.7
α = 0.044	0.063	0.087		

Both groups differ very decidedly in the magnitude of their K-values; that of the strong salts is from 100 to 1000 times as large as the constant which characterizes the weak salts. Lithium chloride, usually regarded as a "strong salt," occupies a position intermediate between these two groups.

TABLE XXXIV

$K = \alpha^2/(1-\alpha)v$ *Applied to Alkylated Amines*

$N(C_2H_5)_2H_2Cl$

v	α	K
660.5	0.0629	6.4×10^{-6}
1189	0.0797	5.8 "
1990	0.100	5.6 "
2388	0.108	5.5 "
3052	0.120	5.3 "
4380	0.139	5.2 "
	Mean = 5.5	

$N(C_4H_9)H_3Cl$

v	α	K
701.7	0.0657	6.6×10^{-6}
1053	0.0776	6.2 "
1762	0.0992	6.2 "
2111	0.1049	5.8 "
2703	0.1168	5.7 "
3877	0.1355	5.5 "
	Mean = 5.8	

$N(C_2H_5)_4$-picrate

v	α	K
1000	0.835	42.6×10^{-4}
5000	0.924	22.1 "
10000	0.946	16.6 "
50000	0.976	8.0 "
100000	0.983	6.0 "

LiCl

v	α	K
100	0.044	2.0×10^{-5}
500	0.091	1.8×10^{-5}
	Mean =	1.9×10^{-5}

Sulphur dioxide as solvent.

The curves given in Fig. 10 represent conductivities of various substances in liquid sulphur dioxide.[1] They show clearly that the peculiar relationships noted in acetone between simple binary salts, which had heretofore been assumed to be alike in their conductimetric behavior, are not linked by chance to the solvent.

A comparative study of the form of the curves in acetone and sulphur dioxide reveals a striking similarity between the two. Even in sulphur dioxide, an inorganic solvent, the tetra-alkylated ammonium halides make up an alto-

[1] Walden and Centnerszwer, Bull. acad. sci., St. Petersburg, 15, 29 (1901).

gether different class of salts from the mono-, di- and tri-alkylated ammonium chlorides. From their conductivities, λ, as well as from the "degree of dissociation" values for

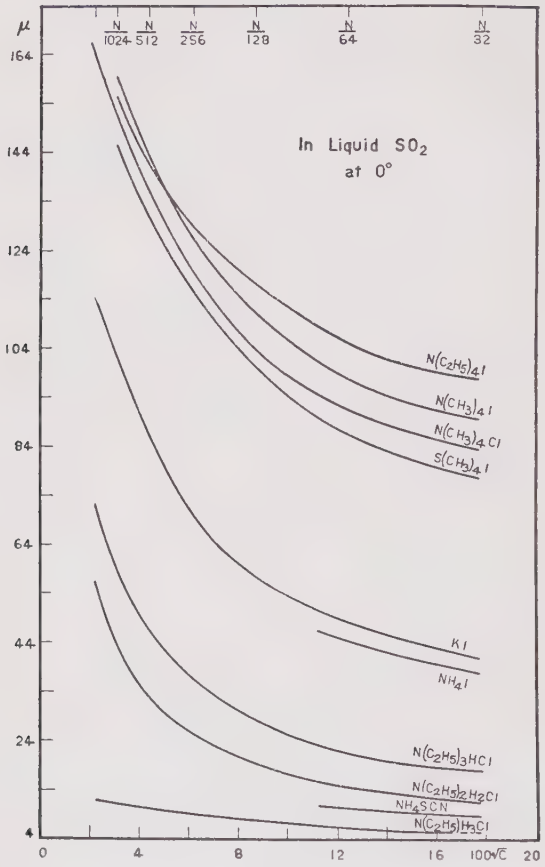


FIG. 10

the dilution range v = 32 to 1024 these substances may be arranged in the following order:

mono-alkylated salts < di- < tri- < tetra-alkylated salts,

and with reference to the anions:

chloride < bromide < iodide.

CHAPTER XI

So-called "Non-conductors" as Ionizing Agents for Typical Binary Salts

> "Non-electrolytes include . . . solutions of all substances in solvents like benzene, carbon disulphide, ether, etc. Solutions in alcohol bridge the gap to electrolytes, as dissociation of salts takes place, even though usually but very slight."
> —Ostwald.[1]

FROM the numerical data presented we have already learned that alcohol brings about appreciable "dissociation" of typical binary salts. The study of solutions in the hydrocarbons and the so-called "non-conductors" like benzene, carbon disulphide, ether, etc., forms a distinctive and much more disputed, yet little investigated field. The experimental difficulty encountered here consisted mainly in the fact, that the usual "test objects," that is the typical binary inorganic salts, were either insoluble in these solvents or too little soluble to yield conclusive results. This field of research therefore appeared to be unsusceptible to either experimental or theoretical treatment.

As late as 1905 the substituted hydrocarbons were regarded by Hantzsch[2] as solvents, which were incapable of ionizing normal dissolved salts. Soon thereafter, however, Walden demonstrated that ethylene chloride, $C_2H_4Cl_2$, dissolved and ionized tetrapropylammonium iodide, $N(C_3H_7)_4I$.[3] Using the mono-, di-, tri-, and tetra alkylated ammonium halides it was subsequently shown that

[1] Ostwald, *Wissenschaftliche Grundlagen der analytischen Chemie*, 54 (1904).
[2] Ber., 38, 1046 (1905).
[3] Walden, Z. physik. Chem., 78, 276 (1911).

methylene chloride, CH_2Cl_2 (dielectric constant, $\epsilon = 8.3$) and chloroform, $CHCl_3$, (dielectric constant, $\epsilon = 4.95$) were also ionizing solvents.[1] Since tetra-isoamylammonium iodide $N(C_5H_{11})_4I$, a typical binary salt, was found to be soluble even in media having a dielectric constant, ϵ, as small as 2.2, it was possible to show that such "non-ionizators" as benzene, C_6H_6, carbon tetrachloride, CCl_4, carbon disulphide, CS_2, and toluene, $C_6H_5CH_3$, could also act as ionizing agents.

Consequently, the poorest solvents, or media having the lowest dielectric constants, were shown to be ionizing solvents. To be sure the form of the conductivity-dilution curves was found to be abnormal in such media. Sometimes both a maximum and a minimum conductivity value could be obtained at higher concentrations; in other instances, only a minimum.

In addition to these peculiarities, other interesting phenomena presented themselves. It was therefore deemed advisable to make a more extended investigation of such solutions. It was found that the individual nature of anions and cations exercised a pronounced influence. Most conspicuous was the effect of the degree of *alkylation* of the ammonium cation upon the conductivity values. The salts

$$RNH_3 \cdot X \rightarrow (R)_2NH_2 \cdot X \rightarrow (R)_3NH \cdot X \rightarrow (R)_4N \cdot X$$

heretofore regarded as equivalent electrolytes, were found not only to conduct, but also to dissociate differently. So pronounced were oftentimes these differences that one could have assumed these salts to be electrolytes of altogether different classes. Conversely, the anions

$$Cl^- \rightarrow Br^- \rightarrow I^- \rightarrow NO_3^-$$

and

$$I^- \rightarrow ClO_4^- \rightarrow SCN^- \rightarrow \text{picrate ion},$$

heretofore analogous in behavior, were found to exercise such an influence upon the degree of dissociation and conductivity that they could be regarded as electrochemically

[1] Walden, Bull. acad. sci., St. Petersburg, 1063 (1912); 789, 1485 (1915).

different and of varied ionizing tendency. The following pages give a general survey of this field, both by λ,v-curves and by the presentation of numerical data.

1. Effect of ϵ on conductivity for chloroform and methylene chloride solutions

Figures 11 and 12, representing methylene chloride and chloroform solutions, bring out clearly the effect of the

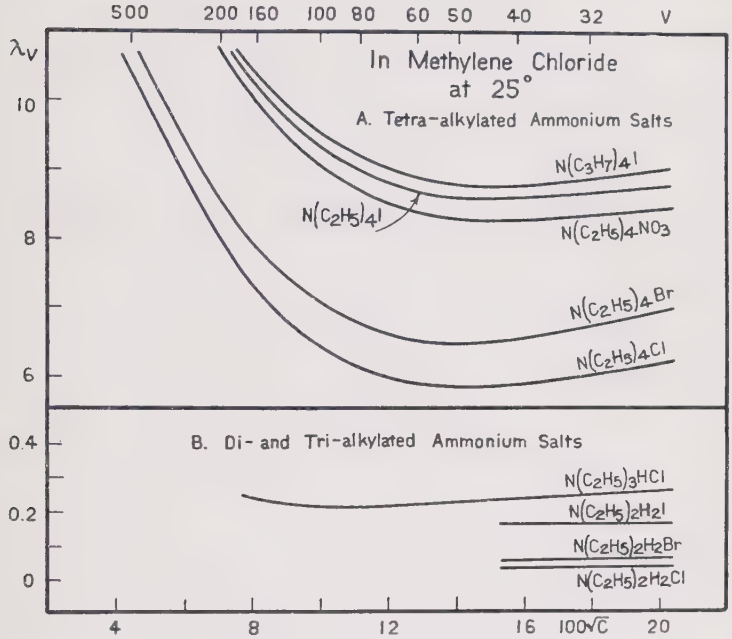


Fig. 11

dielectric constant, ϵ, upon the course of the curves. Tetra-alkylated ammonium salts have been used as solutes and a uniform dilution range, v = 30 to 500 to 1000, has been observed. It is of interest to compare the unique way in which the curves change from those in water (ϵ = 80) to acetone (ϵ = 21.2), sulphur dioxide (ϵ ~ 15), methylene chloride (ϵ = 8.3) and finally chloroform (ϵ = 4.95). Those in water are practically rectilinear. As the dielectric con-

stant becomes less they become more curved, finally those representing solvents with a very small ϵ-value, pass through a definite minimum and then proceed in another predominant direction.

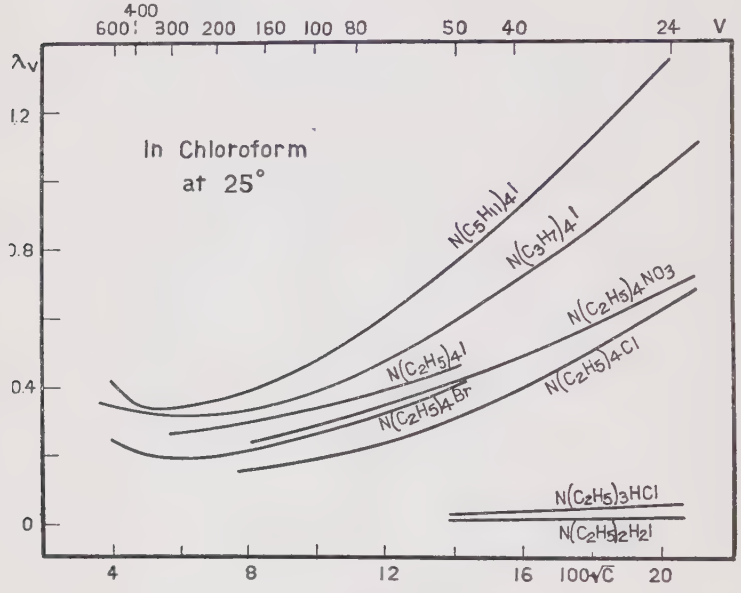


FIG. 12

II. CONDUCTIVITY AND DISSOCIATION IN HYDROCARBONS

The conductivity values in methylene chloride, CH_2Cl_2, chloroform, $CHCl_3$, dichlorethylene, CHCl:CHCl, ethylene chloride, $CH_2Cl{\cdot}CH_2Cl$ and benzene, C_6H_6, are to be presented here.

A. Methylene chloride as solvent, t = 25°

Both[1] the tetra-alkylated, as well as the di- and tri-alkylated, ammonium salts of the halogen hydracids and nitric acid were investigated in this solvent. Table XXXV gives the equivalent conductivities, λ_v, of the tetra-alkylated salts.

[1] Walden, Bull. acad. sci., St. Petersburg, 925 (1913); 1502 (1915).

Table XXXV

*Equivalent Conductivity Values of Various Tetra-Alkylated Ammonium Salts in Methylene Chloride**

Salts	v = 0.75	1.5	2.5	3.0	5.0	10	20	40
$N(C_2H_5)_4Cl$	—	—	—	—	9.49	7.66	6.40	*5.84*
$N(C_2H_5)_4Br$	—	—	11.00	—	9.80	8.30	7.14	*6.67*
$N(C_2H_5)_4NO_3$	—	—	—	—	—	—	8.6	—
$N(C_2H_5)_4I$	—	—	—	—	—	—	8.98	—
$N(C_3H_7)_4I$	6.84	10.69	*11.55*	*11.67*	—	—	9.14	*8.80*
$N(C_3H_7)_3C_2H_5 \cdot I$	—	—	—	—	12.20	10.91	9.73	*9.19*
$N(C_5H_{11})_4I$	—	—	—	—	—	—	9.51	*9.34*

Salts	50	60	75	100	200	400	600	800
$N(C_2H_5)_4Cl$	—	*5.89*	—	6.32	—	—	—	12.2
$N(C_2H_5)_4Br$	*6.43*	*6.74*	—	6.96	8.30	10.45	—	13.8
$N(C_2H_5)_4NO_3$	*8.29*	—	—	9.04	10.69	13.37	—	16.22
$N(C_2H_5)_4I$	*8.62*	—	8.61	9.29	10.89	—	15.44	—
$N(C_3H_7)_4I$	*8.78*	*8.91*	—	9.47	10.95	—	—	—
$N(C_3H_7)_3C_2H_5 \cdot I$	*9.03*	*9.27*	—	9.70	—	—	15.89	—
$N(C_5H_{11})_4I$	—	*9.44*	—	10.1	11.6	15.16	(v = 480)	—

*All solutions were found to be practically colorless. (l.c., 1913).

A closer examination of these numerical results shows the maximum at small dilutions (v = 2 to 3), and always the minimum (italics) where v = 40–60–75. With reference to the numerical value, λ_v, the series

chloride < bromide < nitrate < iodide

expresses its relative size for a given cation both before and after the minimum value.

Behavior of Mono-, Di-, and Tri-alkylated Ammonium Salts.

Let us next study the behavior of the mono-, di-, and tri-alkylated ammonium salts in methylene chloride. In Table XXXVI are given conductivity data obtained by Walden in 1915 (l.c.) for a number of salts.

TABLE XXXVI

Equivalent Conductivities of Various Di- and Tri-alkylated Ammonium Salts in Methylene Chloride, t = 25°

	v = 10	20	40	80
Di-:$N(C_2H_5)_2H_2Cl$	0.045	0.035	0.033	—
$N(C_2H_5)_2H_2Br$	0.0686	0.054	0.0536	—
$N(C_2H_5)_2H_2I$	0.185	0.157	0.160	—
Tri-:$N(C_2H_5)_3HCl$	0.377	0.268	0.236	0.211
Tetra-:$N(C_2H_5)_4Cl$	7.66	6.40	5.84	6.1

These numerical values are of an altogether different order of magnitude than those for the tetra-alkylated salts. For one and the same cation, $N(C_2H_5)_2H_2^+$ the anionic series of λ may again be written as follows:

chloride < bromide < iodide

and the λ-values for the *chlorides* of the various alkylated ammonium bases stand in the relationship

di-alkylated < tri-alkylated < tetra-alkylated salts.

Recalling similar relationships in acetone[1] seems to be sufficient proof that these observations are not due to the chance nature of the solvent.

[1] see p. 237 ff.

Table XXXVII

Conductivities in cis-Dichlorethylene (B.-pt. 58-59°) at $t = 25°$, $\epsilon = 8\text{-}9$

Di-isoamylammonium picrate	$v = 107.4$	142.8	201.4	280.5	336.6
$N(C_5H_{11})_2H_2 \cdot OC_6H_2(NO_2)_3$	$\lambda = 0.0358$	0.0380	0.048	0.056	0.060
Tri-isoamylammonium picrate	$v = 211$	317	422.6	634	950.9
$N(C_5H_{11})_3H \cdot OC_6H_2(NO_2)_3$	$\lambda = 0.199$	0.205	0.214	0.226	0.243
Tetra-isoamylammonium picrate	$v = 34220$	47058	91502	122200	195540
$N(C_5H_{11})_4 \cdot OC_6H_2(NO_2)_3$	$\lambda = 44.60$	47.86	56.33	60.33	66.07

The molecular volumes, V, of these solid salts are the following ($t = 0°$):

$(C_5H_{11})_2NH_2 \cdot OC_6H_2(NO_2)_3$ Mol. wt. = 386, spec. vol. $v_0 = 0.8113$, $V = 313$.
$(C_5H_{11})_3NH \cdot OC_6H_2(NO_2)_3$ " = 456, " = 0.8645, = 394.
$(C_5H_{11})_4N \cdot OC_6H_2(NO_2)_3$ " = 526, " = 0.9009, = 474.

The totally different character of the λ-values therefore can not be ascribed to the differences in these large molecular volumes, V, of the corresponding salts.

B. *Dichlorethylene (cis-form) as Solvent*

The same relationships also are found when an unsaturated hydrocarbon, dichlorethylene (cis) CHCl:CHCl, is chosen as solvent and salts of high molecular weight are investigated.[1]

Evidently these three *picrates* are electrolytes of altogether different natures. Tetra-amylammonium picrate is certainly to be considered as a typical strong salt, whereas the corresponding di-, and tri-amylammonium picrates are extremely weak electrolytes, characterized by their noticeably small conductivities. Here again we have the λ-values in the relationships:

di-alkylated < tri-alkylated < tetra-alkylated salts.

C. *Ethylene Chloride as Solvent.*

Table XXXVIII gives the equivalent conductivities of variously alkylated ammonium salts in ethylene chloride.[2]

It may be emphasized that the two *isomeric* picrates $N(C_2H_5)_3H$-picrate and $N(C_3H_7)_2H_2$-picrate have a different conductivity. Table XXXVIII also compares $N(C_3H_7)_3H$- and $N(C_2H_5)_4$-picrates.

Another method for showing the above differences, uses the α-values

(a) Influence of the anion upon the degree of dissociation of a tetra-alkylated salt.

Cation	Anions			
$N(C_2H_5)_4^+$	Cl^-	I^-	ClO_4^-	picrate ion
$v = 2000$	$\alpha = 0.333$	0.351	0.391	0.470
5000	$\alpha = 0.439$	0.460	0.512	0.593
10000	$\alpha = 0.535$	0.553	0.600	0.686

The tendency towards dissociation is expressed by the anionic series

$$Cl^- < I^- < ClO_4^- <$$ picrate anion

It is worthy of particular attention that the same gradation of anionic effect occurs in the case of the hydrocarbon, $C_2H_4Cl_2$, as was observed previously in the study of acetone solutions.

[1] Walden and Gloy (1927).
[2] Walden and Busch (1927).

Table XXXVIII

Equivalent Conductivity, λ_v, of Alkylated Ammonium Salts in Ethylene Chloride, t = 25°

	v = 1000	2000	5000	10000	∞
Di-ethylammonium chloride	too small to be measureable				experimentally not determinable
Tri-ethylammonium chloride	0.15	0.182	0.312	0.495	
Di-ethylammonium picrate	0.30	0.40	0.59	0.815	
Tri-ethylammonium picrate	—	0.594	0.907	1.35	
Monopropyl ammonium picrate	0.61	0.705	0.933	1.235	
Dipropyl ammonium picrate	0.37	0.461	0.663	0.864	
Tripropyl ammonium picrate	0.49	0.636	0.970	1.410	
Tetra-ethylammonium chloride	—	23.00	30.35	36.99	69.1
Tetra-ethylammonium picrate	—	33.48	42.28	48.92	71.3
Tetra-propyl ammonium picrate	—	31.72	39.62	45.54	62.1
Tetra-ethyl ammonium perchlorate	—	31.84	41.50	48.60	81.0
Tetra-ethyl ammonium iodide	—	26.82	35.16	42.22	76.4

Molecular volumes of $N(C_3H_7)_3H$- and $N(C_2H_5)_4$-picrates may be found as follows (t = 0°):

$N(C_3H_7)_3H$-picrate, mol. wt. = 372, spec. vol. $v_0 = 0.7955$, mol. vol. V = 296

$N(C_2H_5)_4$-picrate, mol. wt. = 385, spec. vol. $v_0 = 0.77$, mol. vol. V = 276

Both picrates have similar molecular volumes, yet at the high dilution v = 10000, the conductivity values are so divergent as $\lambda_{10000} = 1.410$ and $\lambda_{10000} = 48.92$

(b) Influence of the anion upon the degree of dissociation α of di-, and tri-alkylated salts.

Cation $N(C_2H_5)_2H_2^+$	Anion Cl^-	picrate ion
v = 5000	α experimentally not	α = 0.0083
= 10000	α determinable	α = 0.011
Cation $N(C_2H_5)_3H^+$		
v = 5000	α = 0.0045	0.013
= 10000	α = 0.0072	0.019

(The limiting values of λ_∞ were assumed to be those of the corresponding tetra-alkylated salts).

(c) Influence of the degree of alkylation of the cation, v = 10000 liters.

	Anions Cl^-	picrate ion
Di-alkyl. $N(C_2H_5)_2H_2^+$	α = too small	0.011
Tri-alkyl. $N(C_2H_5)_3H^+$	α = 0.0072	0.019
Tetra-alkyl. $N(C_2H_5)_4^+$	α = 0.535	0.686

It is obvious that the ability to dissociate is increased by the presence of the picrate ion even in the case of the di- and tri-alkylated ammonium salts.

When the same anion is employed, the influence of the degree of alkylation upon conductivity values at higher dilutions ($v \leqq 5000$) may be expressed by the series

di-ethyl- < tri-ethyl- < tetra-ethyl ammonium salts

or

dipropyl < monopropyl < tripropyl < tetrapropyl ammonium salt.

It is curious that the same relationship exists here at a dilution of $v \leqq 5000$ liters that was evident in the case of methylene chloride when $v \leqq 10$ liters.

D. *Chloroform*, $CHCl_3$, *as Solvent*, $\epsilon = 4.95$; $t = 25°$

Walden[1] investigated a large number of mono-, di-, and tri-alkylated ammonium salts in this solvent. Several ex-

[1] Bull. acad. sci. St. Peterburg, 789 (1915).

amples are presented in Table XXXIX, together with a number of previously investigated[1] tetra-alkylated salts.

Table XXXIX

Equivalent Conductivities, λ_v, of Tetra-alkylated Ammonium Salts in Chloroform. $t = 25°$

a. Maxima and minima conductivities.

The former are usually to be found in a dilution range of v = 1 to 2 liters, whereas the minima or turning points in the curves appear to be at about v = 300.

Salts	v = 0.75	1,125	1.00	1.50	2.50	5.00
$N(C_2H_5)_4Cl$	—	—	—	—	3.69	2.49
$N(C_2H_5)_4Br$	4.57	—	*4.73*	4.3	3.55	2.43
$N(C_2H_5)_4NO_3$	—	—	—	—	3.36	2.22
$N(C_2H_5)_4I$	—	—	—	—	—	—
$N(C_3H_7)_4I$	2.90	4.44	—	*4.78*	4.58	—
$N(C_5H_{11})_4I$	—	—	—	—	—	—

Salts	v = 10	50	100	300	450	600
$N(C_2H_5)_4Cl$	1.47	0.35	0.21	—	—	—
$N(C_2H_5)_4Br$	1.50	0.42	0.27	*0.21*	*0.21*	0.24
$N(C_2H_5)_4NO_3$	1.36	0.40	0.26	—	—	—
$N(C_2H_5)_4I$	—	0.469	0.35	0.27	—	—
$N(C_3H_7)_4I$	2.00	0.65	—	*0.32*	—	0.34
$N(C_5H_{11})_4I$	—	0.725	0.454	*0.339*	*0.340*	0.388

b. Influence of the anion where the cation remains the same

Tetra-alkylated ammonium cation: $N(C_3H_7)_4 \cdot X$

The λ_v-values stand in the following relationship:

picrate > iodide > nitrate > chloride

Salts	v = 10	20	40
$N(C_3H_7)_4 \cdot Cl$	1.35	0.700	0.380
$N(C_3H_7)_4 \cdot NO_3$	1.77	0.99	0.54
$N(C_3H_7)_4 \cdot I$	2.00	1.213	0.718
$N(C_3H_7)_4$-picrate	2.65	1.6	0.99

[1] Walden, *ibid.*, 922, (1913).

c. Same tri-alkylated cation: $N(C_5H_{11})_3H \cdot X$

A further differentiation in the effect of the various halogen ions is possible here:

thiocyanate > fluoride > bromide > chloride

Salts	v = 10	20	40
$N(C_5H_{11})_3H \cdot Cl$	0.0199	0.00874	0.00620
$N(C_5H_{11})_3H \cdot Br$	0.0365	0.0145	0.0133
$N(C_5H_{11})_3H \cdot F$	0.0766	0.0350	0.0188
$N(C_5H_{11})_3H \cdot SCN$	0.0985	0.0392	0.0185

d. Same di-alkylated cation $N(C_2H_5)_2H_2 \cdot X$.

As in *a* the *anionic* effect may again be depicted by the series

iodide > nitrate ≧ bromide > chloride

Salts	v = 5.0	6.0	10.0	12.0	20.0	24.0
$N(C_2H_5)_2H_2 \cdot Cl$	0.00346	—	0.0018	—	—	—
$N(C_2H_5)_2H_2 \cdot Br$	—	0.0146	—	0.00598	—	—
$N(C_2H_5)_2H_2 \cdot NO_3$	0.037	—	0.012	—	0.0080	—
$N(C_2H_5)_2H_2 \cdot I$	—	0.119	—	0.0308	—	0.0252

Another fact must be emphasized. Let us compare the following chlorides at v = 10:

$N(C_2H_5)_4Cl$	$N(C_3H_7)_3HCl$	$N(C_3H_7)_4Cl$	$N(C_5H_{11})_3HCl$
$= C_8H_{20}NCl$	$= C_9H_{22}NCl$	$= C_{12}H_{28}NCl$	$= C_{15}H_{34}NCl$
$\lambda = 1.47$	0.0304	1.35	0.0199

The size of the cations increases from left to right. Obviously it is not the size of the molecule, but the configuration of the cations—symmetrical arrangement of the alkyls—which influences the conductivity values.

TABLE XL

Influence of the degree of alkylation of cations where the anion remains the same.

(a) Anion $X^- = Cl^-$; $t = 25°$, $v = 10$.

	$R = C_2H_5$	$R = C_3H_7$
Di-substituted salt, $HN(R)_2HCl$	$\lambda = 0.0018$	0.00085
Tri-substituted salt, $N(R)_3NCl$	$\lambda = 0.0338$	0.0304
Tetra-substituted salt, $N(R)_4Cl$	$\lambda = 1.47$	1.35

(*b*) *Anions* $X^- = Cl^-, Br^-, NO_3^-$ *or* I^-; $t = 25°$, $v = 10$

	Cl^-	Br^-	NO_3^-	I^-
Di-ethyl salt $(C_2H_5)_2NH_2 . X$	$\lambda =$ 0.0018	0.00885	0.012	0.060
Tri-ethyl salt $(C_2H_5)_3NH . X$	$\lambda =$ 0.0338	0.108	0.198	0.256
Tetra-ethyl salt $(C_2H_5)_4N . X$	$\lambda =$ 1.47	1.50	1.36 ≷ 1.5	

In (*a*) the tri-substituted salt $N(C_2H_5)_3HCl$ is isomeric with the di-substituted $N(C_3H_7)_2H_2Cl$. Both salts have practically the same size, nevertheless their λ-values are different. The effect of the degree of alkylation upon the λ-values may be expressed by the series:

di-substituted < tri-substituted < tetra-substituted ammonium salt.

In (*b*) for every one of the anions the effect upon the λ-values is analogous:

di-substituted < tri-substituted < tetra-substituted salt.

At the same time, however, we recognize another effect when these salts are compared with one another with reference to the specific action of the anions. It is obvious that the influence of the nature of the *anions* varies with the degree of alkylation of the ammonium cation. If we consider, for instance, the two extremes, chloride and iodide, it will become evident that, as the number of alkyls bound directly to the nitrogen increases, the numerical size of the λ-values, or the tendency of salts towards ion formation, becomes more uniform. Several conclusions may be drawn with reference to this specific effect of the chloride and iodide anions:

(1) that this effect is practically of the same order in the case of the tetra-alkylated ammonium salts (about 1 : 1.5)

(2) that it is greatest in the case of the di-alkylated cations (λ = 0.0018 and 0.060, or 1 : 30)

(3) that it is intermediate in the case of the tri-alkylated cations (λ = 0.0338 and 0.256, or 1 : 8)

E. *Benzene as Solvent.*

The last solvent to be considered is a hydrocarbon and a typical nonconductor, namely benzene whose di-electric constant $\epsilon = 2.19$ at 72°. This medium represents the extreme limit of ionizing solvents.

Experiments were all carried out at 72° in order to increase the solubility of the various salts. The difficult problem of finding typical binary salts soluble in benzene was readily solved by selecting the tetra-isoamylammonium salts, $N(C_5H_{11})_4X$, as solutes. Equivalent conductivities of several of these salts in benzene are presented in Table XLI (Walden and Gloy, 1927).

TABLE XLI

Equivalent Conductivities of Various Tetra-isoamylammonium Salts in Benzene at 72°

$N(C_5H_{11})_4.I$		$N(C_5H_{11})_4.ClO_4$		$N(C_5H_{11})_4.SCN$		$N(C_5H_{11})_4$-picrate	
v	λ	v	λ	v	λ	v	λ
13.0	0.072	13.9	0.098	5.0	0.207	40.3	0.14
16.4	0.040	17.4	0.076	13.8	0.118	48.3	0.105
19.9	0.039	20.45	0.058	20.7	0.0875	60.4	0.071
24.3	0.034	26.06	0.046	24.9	0.0748	72.4	0.051
29.2	0.023	32.1	0.034	31.02	0.0550	91.4	0.038
36.4	0.021	38.6	0.024	37.4	0.0475	108.7	0.027
43.8	0.017	46.4	0.018	51.6	0.0409	—	—

The conductivities λ_v decrease in all cases with increasing dilution v and in practically the same ratio. The λ_v-values at the same dilution, v = 40, may be represented by the series

$$\begin{array}{ccccccc} \text{iodide} & < & \text{perchlorate} & < & \text{thiocyanate} & < & \text{picrate} \\ 0.019 & < & 0.023 & < & 0.046 & < & 0.14 \end{array}$$

Particularly deserving of attention is the fact that the anionic effect on the size of the λ-values in benzene, a "non-conductor," is the same as that on α in acetone and ethylene chloride.

The temperature coefficient, c, of the conductivity in this medium is also of interest. The salt $N(C_5H_{11})_4SCN$ may serve to illustrate this fact.

	v = 15.8	23.7	35.6
$t_1 = 25°$	$\lambda = 0.0337$	0.0230	0.0131
$t_2 = 72°$	$\lambda = 0.105$	0.0751	0.0496
$c = \frac{1}{\lambda_{t_1}} \frac{(\lambda_{t_2} - \lambda_{t_1})}{(t_2 - t_1)}$	$= 0.045$	0.048	0.059

Viscosity of benzene, η, $t_2 = 80°$, $\eta_{t_2} = 0.003358$

$t_1 = 70°$, $\eta_{t_1} = 0.003591$

Temperature coefficient, $a = \frac{(\eta_{t_2} - \eta_{t_1})}{(t_2 - t_1)} \frac{1}{\eta_{t_1}} = -0.0648$

The temperature coefficient, c, of conductivity is in this case positive; the negative temperature coefficient, a, of viscosity is of the same order of magnitude.

No new anomalies in the course of the conductivities with increasing dilution or change in temperature, are met here. The behavior of solute and solvent must be regarded as normal. Decrease in equivalent conductivity with increasing dilution is a phenomenon which is characteristic of all media with small dielectric constants in the range of slight dilution.

The figures given above are of fundamental importance for several reasons: first, typical strong binary salts conduct in benzene solution; secondly, conductivity varies with the salt and with the nature of the anion; third, the gradation of anions as based on their conductivities corresponds to that noted previously in the case of strong ionizing agents; fourth, conductivity increases with rise in temperature. Salt solutions in benzene, like normal electrolytes in solution, have a positive temperature coefficient of conductivity of the same order of magnitude as the temperature coefficient of viscosity.

It may be mentioned in this connection that chemical ionic reactions seem to take place promptly in benzene solutions. An immediate precipitate is obtained when

solutions of tetra-isoamylammonium iodide or thiocyanate are mixed with silver perchlorate which also conducts the electric current in benzene.

$$N(C_5H_{11})_4{}^+I^- + Ag^+ClO_4^- = AgI + N(C_5H_{11})_4{}^+ClO_4^-$$

We might go still further and calculate the "degree of dissociation," $\alpha = \lambda_v/\lambda_\infty$, of salts in this "non-conductor." Later we shall learn of a formula which correlates the maximum conductivity λ_∞ of a given complex salt with the viscosity η of any desired solvent, namely

$$\lambda_\infty \cdot \eta = \text{constant.}$$

For $N(C_5H_{11})_4$-picrate $\lambda_\infty \cdot \eta = 0.424$. The maximal conductivity, λ_∞, of this salt in benzene theoretically would then have to be

$$\lambda_\infty = 0.424/\eta$$

The viscosity of benzene at 72° is $\eta = 0.00354$ (Thorpe and Rodger). The limiting conductivity for tetra-isoamylammonium picrate would then be

$$\lambda_\infty = \frac{0.424}{0.00354} \sim 120 \text{ (at } 72°)$$

From these figures the approximate values for α may now be determined with ease.

$N(C_5H_{11})_4 \cdot C_6H_2(NO_2)_3O$ in benzene at 72°.

$v =$	40.3	48.3	60.4	∞
$\lambda_v =$	0.14	0.105	0.071	120
$\alpha =$	0.00117	0.00088	0.00059	—

Naturally the true significance of these figures is masked in view of the decrease in λ-values with increasing dilution. However, from analogy with the other "poor" ionizing agents thus far discussed, it may be stated that typical salt-electrolytes exhibit conductivity, ionic dissociation and normal ionic reactions in benzene solution.

III. At what dilutions does the minimal equivalent conductivity appear?

This question has been discussed repeatedly by Walden,[1] who set up the following empirical formula for determining the characteristic dilution, v, for the minimum equivalent conductivity:

$$v_{min} = (K/\epsilon)^3,$$

where K is a characteristic constant for typical binary salts ($K = 32 - 37$) and ϵ the dielectric constant for the solvent in question.

The examples given in Table XLII show the degree of agreement between the computed and the experimentally observed v_{min}, in the electrolite $AgNO_3$.

Salts: *Tetra-alkylammonium halides* $(R)_4NX$
(compare with former tables)

in chloroform, $t = 25°$, $\epsilon = 4.95$:
Minimum observed at $v \sim 300$ l.
Minimum calc. $v = (33/4.95)^3 = 296$.

in methylene chloride, $t = 25°$, $\epsilon = 8.3$:
Minimum observed $v = 40 - 75$ l.
Minimum calc. $v = (33/8.3)^3 = 63$.

in phenol[2] C_6H_5OH, $t = 50°$, $\epsilon = 9.58$:

Salt: $N(CH_3)_4I$:

$v = 20.0$	$\lambda = 2.887$		
28.2	2.822		
37.7	2.823	min.	$v_{calc.} = (33/9.58)^3 = 40$
78.2	3.074		

A minimum shows up both in the case of salts composed of small elementary ions, and in salts composed of extremely large, organic ions, which do not tend toward solvation. Thus, [see p. 272].

[1] Bull. acad. sci. St. Petersburg, 907, 987, 1075 (1913). *Also* Z. physik. Chem., **94**, 295 (1920).
[2] Kraus and Kurtz, J. Am. Chem. Soc., **44**, 2465 (1922).

TABLE XLII
Electrolyte—Silver Nitrate

Solvent	Temp. t	Dielectric Constant ϵ	Dilution v	Molecular conductivity λ_v	Calc. for v_{min} $(K/\epsilon)^3 = (33/\epsilon)^3$
Methylamine CH_3NH_2	15	10	20.7	19.55	
F. F. Fitzgerald,			*30.5*	18.68 } Min.	36
J. Phys. Chem.,			*40.5*	18.41 }	
16, 630 (1912).			59.6	18.89	
Ethylamine $C_2H_5NH_2$	15	6.17	31.4	1.19	
F. F. Fitzgerald,			62.7	0.96	
loc. cit.			*125.0*	0.854 Min.	150
Aniline $C_6H_5NH_2$	25	7.2	26.4	corr. 0.37	
Sachanov, Z.			32.6	0.35	
physik. Chem., 83, 140			*53.4*	0.33 } Min.	96
(1913).			*112.9*	0.33 }	
			186.6	0.37	
Quinoline C_9H_7N	25	8.9	7.2	corr. 3.17	
Sachanov, loc. cit.			13.5	2.90	
			35.7	2.81 } Min.	51
			92.7	3.08 }	
Benzylamine $C_7H_7NH_2$	25	5.2	>80	—	256
Sachanov (1916).					
Pyridine C_5H_5N	25	12.56	23.56	30.6	
Sachanov (1916).			*15.46*	30.1 Min.	18
			6.37	30.4	
m-Chloraniline $C_6H_4ClNH_2$	25	13.35	*27.54*	0.844 } Min.	15
Sachanov (1916).			*11.80*	0.779 }	
			4.42	0.945	

Table XLII (Continued)

Electrolyte—Silver Nitrate

Solvent	Temp. t	Dielectric Constant ϵ	Dilution v	Molecular conductivity λ_v	Calc. for v_{min} $(K/\epsilon)^3 = (33/\epsilon)^3$
4 Vol. Aniline + 1 Vol. Pyridine Sachanov (1916).	25	8.0	61.3	3.85 Min.	70
			47.9	3.79	
			27.3	3.96	
1 Vol. Aniline + 1 Vol. Pyridine Sachanov (1916).	25	9.7	62.1	11.9 } Min.	39
			35.85	11.4 }	
Ammonia NH_3 Franklin, Z. physik. Chem., 69, 288 (1909).	−33.5	22	10.540	corr. 121.5*	
			6.180	" 119.3	
			3.624	" 118.9 Min.	3.4
			1.689	" 124.5	
1 Vol. Acetonitrile + 2 Vol. Pyridine Sachanov (1916).	25	19.7	*5.55*	53.1 Min.	4.7
			2.27	47.3	
			1.87	47.5	
Acetonitrile CH_3CN Sachanov (1916).	25	35.8	1.630	44.5	
			1.076	41.6 Min.	0.8
			0.593	44.4	
1 Vol. Acetonitrile + 1 Vol. Water Sachanov (1916).	25	59.7	1.644	80.7	
			0.883	78.5	
			0.547	78.9	
The λ-values of Sachanov, or v reduced to $(v - v_s)$ where $v_s = M(AgNO_3)/d$			1.605	$\lambda' =$ 78.8	
			0.844	75.0	
			0.508	73.2	0.2

*Walden, Z. physik. Chem., **94**, 295 (1920).

Tetra-isoamylammonium picrate $N(C_5H_{11})_4O{\cdot}C_6H_2(NO_2)_3$

in dichlorethylene ($C_2H_2Cl_2$) $t = 25°$ }
(Walden and Gloy) $\epsilon = 9.22$ }

$v =$	17.4	26.15	39.22	58.84	88.26	670
$\lambda =$	8.28	*8.05*	*7.93*	*8.06*	8.38	12.62

Calc. $v_{min.} = (32/9.22)^3 \sim 42$ l.

in pentachlorethane (C_2HCl_5) $t = 25°$ }
(Walden and Gloy) $\epsilon = 3.76$ }

$v =$	14.7	74.4	171.5	286
$\lambda =$	0.17	0.030	0.0125	0.0108
$v =$	343	429	572	715
$\lambda =$	*0.0106*	*0.0105*	*0.0107*	0.0112

Calc. $v_{min.} = (32/3.76)^3 = 600$ liters

In benzene solutions ($t = 72°$, $\epsilon = 2.19$) a minimum should occur in the dilution range $v_{min.} = (32/2.19)^3 \sim 3100$ liters. No experimental proof of this supposition has as yet been made.

SUMMARY

Experimental evidence has been presented to prove that certain hydrocarbons, usually considered to be "non-conductors," are good solvents and also ionizing media for typical binary salts. Conductivity measurements of solutions in (1) methylene chloride CH_2Cl_2 ($\epsilon = 8.3$), (2) chloroform $CHCl_3$ ($\epsilon = 4.95$), (3) di-chlorethylene (cis-form) CHCl:CHCl ($\epsilon = 8$–9?), (4) ethylene chloride $CH_2Cl{\cdot}CH_2Cl$ ($\epsilon = 10$), and benzene C_6H_6 ($\epsilon = 2.19$), some saturated and others unsaturated hydrocarbons, have been presented. The whole field of ionizing media has been studied since the usual series of liquid compound solvents is limited by the dielectric constants $\epsilon_{25} = 80$ for water and $\epsilon_{25} = 2.2$ for benzene.

The alkylated ammonium salts have been employed as typical binary salts and these have been studied with reference to their conductivity, λ_v, both in moderately dilute solutions and also at the very highest dilutions. In

certain cases the maximal equivalent conductivities λ_∞ were extrapolated and the "degree of dissociation" $\alpha = \lambda_v/\lambda_\infty$ calculated.

The differentiation of supposedly similar alkylated ammonium salts, as proved for acetone solutions, was found to be a normal phenomenon in these hydrocarbons. These salts fall sharply into two classes: the tetra-alkylated ammonium salts which conduct the current well and the other group, comprising the di-, tri,- and mono-alkylated salts which conduct only moderately or very poorly. The series

tetra- > *tri-* (*mono-*) > *di-alkylated ammonium salt*

expresses the relationship in conductivity and percentage dissociation values at equivalent dilution.

The *degree of alkylation*, or the constitution of the ammonium cation has a very profound influence upon the dissociability (α) of a salt. Thus, at a dilution v = 10000 (t = 25°) the following data are obtained in ethylene chloride as solvent

$(C_2H_5)_2NH_2 \cdot Cl$	$(C_2H_5)_3NH \cdot Cl$	$(C_2H_5)_4N \cdot Cl$
α = immeasurably small	0.0072	0.535

The differences between the tetra-alkylated ammonium salts (particularly the chlorides) on the one hand, and the di- and tri-alkylated salts on the other, are so large that it would indeed be permissible to speak of them as entirely different electrolytes. Conversely, these differences might be used to ascertain the *constitution* of such salts.

The individual nature of the *anions* in these solvents is also differentiated very sharply. The anionic effect upon the λ- and α-values when the cation remains the same, is expressed by the series:

picrate ion > ClO_4^- > I^- > NO_3^- > Br^- > Cl^-

It must be said, however, that the nature or chemical constitution of the cation exerts the greater effect upon the

electrolytic character of a binary salt. A salt composed of the most active anion, the picrate ion, and a slightly active cation, such as $N(C_2H_5)_2H_2^+$ or $N(C_2H_5)_3H^+$, is dissociated to nowheres near as great an extent as one made up of a cation, such as $N(C_2H_5)_4^+$, and a very slightly active anion, Cl^-. This point may be illustrated by data for ethylene chloride solutions, at v = 10000:

$N(C_2H_5)_2H_2^+$-picrate	$N(C_2H_5)_3H^+$-picrate	$N(C_2H_5)_4^+Cl^-$
$\alpha = 0.011$	$\alpha = 0.019$	$\alpha = 0.535$

It seems necessary to assume in the case of alkylated ammonium salts, a separation into strong and weak salts in much the same manner as acids are classified. Just as stepwise chlorination of a weak carboxylic acid results, in the case of acetic acid, in the successive formation of the increasingly stronger mono-, di-, and trichloracetic acids, so does stepwise alkylation of the ammonium radical lead from a "weak" cation to a "strong" tetra-alkylated $(R)_4N^+$ cation which in combination with anions gives compounds that may be regarded as typical strong salt-electrolytes in all solvents.

Since the molecules of these salts, especially the chlorides, are associated in all solvents with small di-electric constants one may suppose that stepwise dissociation with preliminary formation of complex ions takes place. The size of the alkyls and the degree of alkylation influence not only the degree of symmetry of the cations, but they also affect the small chlorine atom which, as acceptor of an electron, may be so located with reference to the center of the positive charge of the salt molecule, that the tendency to sever the bond or the proneness of the solvent to take up the anion may be decidedly lessened. It may furthermore be assumed in the case of the mono-, di- and tri-alkylated ammonium salts that the hydrogen chloride, HCl, is held by what might be called a semipolar, not a heteropolar, bond and consequently exhibits the behavior of moderately strong organic acids. The following facts are of interest in

this connection. At 150° and in the *molten* state[1] the molecular conductivities, λ, for the salts listed below are:

			λ^{150}
mono :	$(C_3H_7)NH_3 \cdot OC_6H_2(NO_2)_3$		1.311
tri :	$(C_3H_7)_3NH$	"	1.352
di :	$(C_3H_7)_2NH_2$	"	2.484
tetra :	$(C_3H_7)_4N$	"	5.189

It is obvious that even in the molten state the tetra-alkylated ammonium salt has the highest conductivity and the mono-alkylated, the lowest λ. The λ-values increase in the order:

mono- < tri- < di- < tetra-alkylated cation.

The phenomenon of the minimum equivalent conductivity is regarded as a normal fact in widely differing solvents and is calculated approximately by an empirical formula.

[1] Walden, Ulich and Birr, Z. physik. Chem., 131, 14, (1927).

CHAPTER XII

Regularities in Maximal Conductivities and Ion Mobilities in Non-aqueous Solvents

OUR considerations thus far have given sufficient experimental basis to warrant a search among the abundance of data on hand for any regularities common to all solvents. In view of the fact that aqueous solutions have been investigated so carefully, the laws which govern their behavior may be used as patterns. However the larger number of non-aqueous solvents presented new types of problems, which suggested a search for new relationships between the maximal conductivity λ_∞ and the other physical properties of each individual solvent.

The following questions only, will be considered in detail:

(A) Is the Kohlrausch law of the independent mobility of ions valid in non-aqueous solvents, and may it be applied to complex cations and anions?

(B) What causes the great differences in limiting conductivities λ_∞ of the same salt in the various solvents? (Maximal conductivity and viscosity).

(C) What is the relation between ion mobilities and viscosity?

(D) How may ion mobilities be deduced from the maximal conductivities?

(A) the kohlrausch law of the independent mobility of ions in non-aqueous solvents

> "Very seldom does one arrive at a limiting value. The law of the independent mobility of ions is fulfilled only approximately or not at all."
> —Kohlrausch and Holborn, 1916.

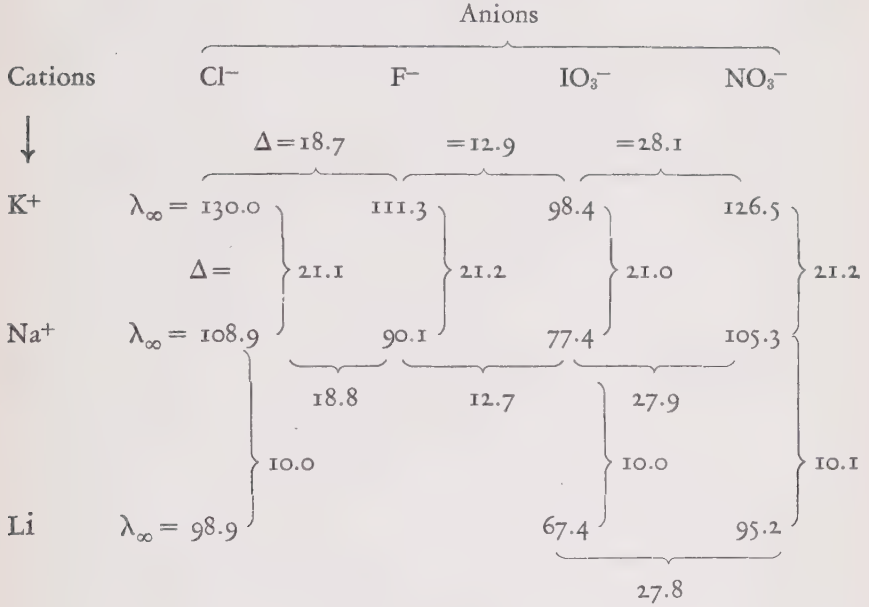
Thus Kohlrausch and Holborn[1] criticized limiting values, λ_∞, and the law of independent mobility of ions in

[1] *Das Leitvermögen der Elektrolyte*, p. 110 (2d ed., 1916).

non-aqueous solvents. No statement will be made here as to whether, or to what extent this criticism of the many recorded conductivity investigations was justified in 1916. That such a remark is at present out of date and contrary to both the old and new facts at hand, is particularly to be

TABLE XLIII

Maximal Conductivities of Typical Binary Salts In Water. $t = 18°$



emphasized. Since experimental methodology has been made decidedly more sensitive, it is now possible to carry out measurements even to the highest dilutions. The limiting conductivities, λ_∞, for typical binary salts can now be readily determined even in such poor ionizing media as the hydrocarbons. Furthermore it can be demonstrated, with the aid of the λ_∞-values, that the Kohlrausch law applies as precisely to non-aqueous, as it does to aqueous solutions.

TABLE XLIV

Maximal Conductivities of Typical Binary Salts in Methyl Alcohol. $t = 25°$[1]

Cations:		Li⁺	Na⁺	K⁺	Rb⁺	Cs
Anions	Nitrate $\lambda_\infty =$	100.25	106.45	114.55	118.15	122.95
		$\Delta = 6.20$	8.10	3.60	4.80	
	Chloride $\lambda_\infty =$	90.90	96.95	105.05	108.65	113.60
		$\Delta = 6.05$	8.10	3.60	4.95	
	$(NO_3^- - Cl^-) =$	$\overline{9.35}$	$\overline{9.50}$	$\overline{9.50}$	$\overline{9.50}$	$\overline{9.35}$

TABLE XLV

Maximal Conductivities in Acetone Solution. $t = 25°$[2]

		Picrate⁻	Perchlorate⁻	
Tetra-ethylammonium⁺	$\lambda_\infty =$	177.3	208.7	
	-9.7	$\Delta = -31.4$		-9.8
Tetramethylammonium⁺	$\lambda_\infty =$	187.0	218.5	
	11.0	$\Delta = -31.5$		11.2
Diphenyl guanidinium⁺	$\lambda_\infty =$	176.0	207.3	
		$\Delta = -31.3$		

[1] Frazer and Hartley, Proc. Roy. Soc. London, **A109**, 362 (1925).
[2] Walden, Ulich and Busch, Z. physik. Chem., **123**, 465 (1926).

Let us first illustrate the applicability of this law, using the limiting values obtained by Kohlrausch in his measurements on aqueous salt solutions at 18°C. This also will give us a standard of comparison for the behavior of these salts in non-aqueous solvents.

The λ_∞-values used in TableXLIII are those observed by Kohlrausch.[1]

In Tables XLIV–XLVIII the limiting conductivities, λ_∞, have been uniformly extrapolated by the square-root formula $\lambda_\infty = \lambda_v + a\sqrt{c}$.

TABLE XLVI*

Maximal Conductivities in Ethylene Chloride, $C_2H_4Cl_2$, t = 25°

Anions:	picrate⁻	iodide⁻	perchlorate⁻	
$N(C_2H_5)_4^+$ Tetra-ethyl-ammonium⁺	71.3	76.4	81.0	
		−5.1	−4.6	
9.2		=9.1		= 9.2
$N(C_3H_7)_4^+$ Tetrapropyl-ammonium⁺	62.1	67.3	71.8	
		−5.2	−4.5	
8.1				= 8.2
$N(C_5H_{11})_4^+$ Tetra-isoamyl-ammonium⁺	54.0	−9.6	63.6	

* Walden and Busch, unpublished measurements (1927).

Ethylene chloride, as an ionizing agent, is of particular interest since it represents a hydrocarbon, a so-called "non-conductor," whose di-electric constant is $\epsilon = 10$. Later we shall present examples in water at 0° ($\epsilon = 88.2$) which will for the first time demonstrate *the applicability of the Kohlrausch law for the range of solvents between* $\epsilon = 10$ *and* $\epsilon = 88.2$.

[1] Z. Elektrochem., 13, 342 (1907).

From the mass of older data on hand several series of measurements have been chosen and are given below in Table XLVII. The limiting values, λ_∞, have been determined by the $\sqrt{c}$-formula and converted into reciprocal ohms.

TABLE XLVII

Maximal Conductivities in Various Solvents

(a) Acetonitrile,[1] CH_3CN, t = 25°

Anions:	Cations: Na^+	K^+	$N(C_2H_5)_4^+$	$N(CH_3)_4^+$
Br^-	—	—	185	
			Δ=10	
	Δ=8			
I^-	190	198	195	210 (?)
	Δ=16		17	12
SCN^-	206	215	—	223
		Δ=9		8

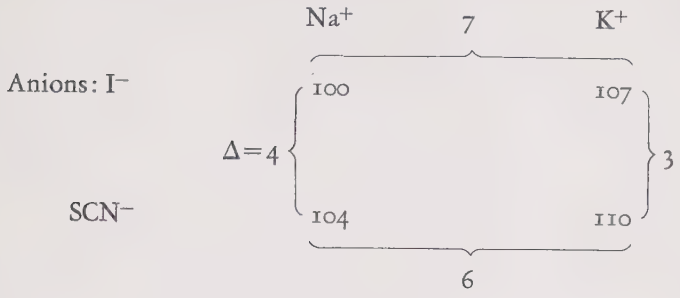
(b) Epichlorhydrine,[2] $CH_2Cl{\cdot}CH{\cdot}CH_2$ (O), t = 25°

Cations:	Anions: Cl^-	Br^-	I^-	
$N(CH_3)_4^+$	64.6	68.0	68.2	
	Δ=4.2	= 3.6		= 4.2
$N(C_2H_5)_4^+$	60.4	(63.8)	64.0	
	Δ=3.4	= 3.6		
$N(C_3H_7)_4^+$	57	—	—	

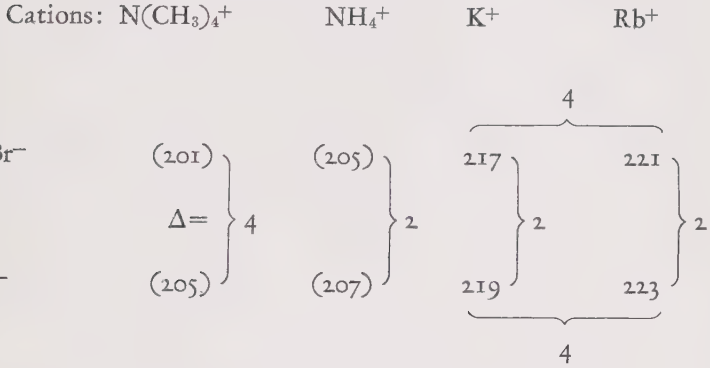
[1] Walden, Z. physik. Chem., **54**, 185 (1905).
[2] *Idem*, 216.

TABLE XLVII (Continued)

(c) Pyridine, C_5H_5N. $t = 50°$ [1]



(d) Sulphur dioxide SO_2. $t = -15°$ [2]



(e) Ammonia, NH_3, $t = -33.5°$ [3]

	Cl^-	Br^-	I^-	NO_3^-	BrO_3^-
Li^+	—	—	—	283	—
Ag^+	—	—	287	287	—
Na^+	309	302	301	301	278
NH_4^+	310	303	302	302	—
Tl^+	—	—	—	323	—
K^+		340	339	339	—

[1] Dutoit and Ottiker, Thesis, Lausanne (1907).
[2] Gyr, Thesis, Lausanne (1907).
[3] Franklin and Kraus, J. Am. Chem. Soc., **27**, 219 (1905). The limiting values are from the smoothed ones by Kraus and Bray, J. Am. Chem. Soc., **35**, 1368 (1913).

It may be noted further that the limiting values in liquid ammonia at $-33.5°$ are practically the same as those in water at 80–85°. (If the limiting values λ_∞ be cal-

TABLE XLVIII

*Maximal Conductivities in Water**

(a) t = 100°

	Cl^-	ClO_4^-	NO_3^-	picrate$^-$
			82	
K^+	406	375	385	293
	Δ=46	21	Δ=46	
Na^+	360	79	339	Δ=97
		21		
Li^+		296		214
		Δ=82		

(b) t=0°

	Cl^-	ClO_4^-	picrate$^-$
K^+	81.8	77.7	55.5
	Δ=14.5	Δ=22.2	
Na^+	67.3	21.3	Δ=21.3
Li^+		56.4	34.2
		Δ=22.2	

* Walden and Ulich, Z. physik. Chem., 106, 76 (1923).

culated from the data of Franklin and Kraus, using the $\sqrt{c}$-formula, figures are obtained which are from 15 to 20 units larger than those given above.) Table XLVIII is appended to bring out the numerical relationships of λ_∞-values in water at 100° and 0°.

SUMMARY

The Kohlrausch law has been tested with reference to its applicability to the equivalent conductivities λ_∞, calculated for infinite dilutions, $v = \infty$, by means of the square-root formula. It has been found to hold:

(1) in aqueous solutions up to 100°, as well as in non-aqueous solutions between $t = -33.5$ to $+50°$,

(2) for both elementary univalent cations and anions, as well as for large univalent organic ions,

(3) for both non-aqueous solvents with high di-electric constants and pronounced dipolar character such as the alcohols and ammonia, as well as for the so-called non-conductors, the halogen hydrocarbons, as ethylene chloride, with $\epsilon \leqq 10$.

(B) MAXIMAL CONDUCTIVITY AND VISCOSITY.

$\lambda_\infty \cdot \eta = \text{constant}$, or $l_K \cdot \eta = K_1$; $l_A \cdot \eta = K_2$.

Even since 1906 Walden[1] has sought to prove that the product of the maximal conductivity, λ_∞, of a given typical binary salt and the viscosity, η, of the pure solvent is constant,

(1) at various temperatures in a given solvent

$$\frac{d(\lambda_\infty \cdot \eta)}{dt} = 0,$$

(2) For different solvents and a given electrolyte

$$\lambda^t_\infty \cdot \eta^t = \text{constant}.$$

The first of these relationships implies that the temperature coefficient of the molar conductivity, λ_∞, is equal to the negative value of the temperature coefficient of the viscosity, η, of the pure solvent, or

$$\frac{1}{\lambda_\infty} \cdot \frac{d\lambda_\infty}{dt} = -\frac{1}{\eta} \cdot \frac{d\eta}{dt}$$

The second of these relations determines the numerical value of the maximal conductivity, λ_∞, at infinite dilution,

[1] Z. physik. Chem., **55**, 246 (1906).

$v = \infty$ (or $c = 0$), and implies that the limiting conductivity is in general directly proportional to the viscosity or internal friction, η, of the solvent employed.

These relationships were deduced by Walden as empirical rules quite *independent* of theoretical considerations of any sort. They imply that free ions are simply and visibly hindered in their passage by the cohesive forces of the solvent. A survey of the views accepted by the leading electrochemists of that day shows that the idea of such a mutual relationship was a scientific *novum*. Writing with reference to the rôle of the di-electric constant which, according to Nernst and Thomson (1893), determined the dissociation power of a medium, *Abegg*[1] *says* "for example . . . it was to be expected that the solutions in benzonitrile and propionitrile (with $\epsilon = 26.0$ or 26.5) would be equally dissociated and consequently would show about the same conductivity. However, a comparison by Schlundt (1901) of the conductivities of silver nitrate in these two di-electrically equal solvents, as measured by Lincoln and Dutoit, revealed large differences. The conductivity in propionitrile would seem to indicate a markedly greater ionic concentration." Thus for $AgNO_3$ in:

Benzonitrile		Propionitrile		Pyridine	
v	λ	v	λ	v	λ
32	9.0	32	36.1		
59	11.9	63.7	48.8	61	32.1
152	17.4			141	38.5
$\epsilon = 26.0$		$\epsilon = 26.5$		$\epsilon = 12.4$	

It is argued that, since propionitrile and benzonitrile have practically equal di-electric constants, they should dissociate to an equal degree; consequently a given salt should possess the same conductivity in both solvents. Apparently the degree of dissociation α $(=\lambda_v/\lambda_\infty)$, has been confused with the conductivity, λ_v, despite the fact that the former is based upon the ratio λ_v/λ_∞ and α remains

[1] *The Electrolytic Dissociation Theory*, p. 149 (New York, 1907).

the same even if λ_v/λ_∞ is changed n times, becoming $n\lambda_v/n\lambda_\infty$.

The same mistaken conception is also found in Jahn's excellent book.[1] He mentions as an evident contradiction to the rule that "ethyl acetate, which in spite of its small di-electric constant (6.5) nevertheless yields solutions which conduct fairly well; at least as well as those of ethylcyanacetate which has a much larger di-electric constant (26.7)."

Abegg is cognizant of this erroneous argumentation for he says: "The conductivities depend not only upon the degree of dissociation, but also upon the mobility of the ions; this mobility stands in an entirely unknown relation to the nature of the solvent." However, Jahn himself admits that "the deduction of the conductivity from the degree of dissociation is not very rigid," as conductivity is dependent not only upon α, but also upon the mobility of the ions. "Unfortunately, up to the present we know nothing at all concerning the connection between these mobilities and the chemical nature of the solvent, and can predict nothing even theoretically, concerning it."

Thus, as late as 1905–1907 the true significance of conductivity values λ_v in their relation to the classical degree of dissociation was still very obscure and uncertain. According to Abegg and Jahn nothing definite could be stated, either experimentally or theoretically, concerning the relation between the mobility of the ions and the properties of the solvent. Under such circumstances any attempt to throw light upon this question by introduction of new facts was indeed to be designated as a distinct and very desirable advance.

Walden's "Internal Friction and Its Relation to Conductivity"[2] contained the numerical results of his own measurements, namely:

(1) The maximal conductivities (extrapolated in accordance with the cube root formula) of $N(C_2H_5)_4I$, chosen

[1] *Grundriss der Elektrochemie*, p. 201, 209 (Wien, 1905).

[2] Concluded in October 1905.

as the "normal salt" or electrolyte in more than thirty solvents at the temperatures $t = 0°$ and $25°$.

(2) The viscosities η of all of these solvents at the same two temperatures.

The temperature coefficients for both of these fundamental magnitudes were determined, with the result that

(1) The temperature coefficient of the maximal conductivity, λ_∞, is always positive.[1] The smaller the limiting value, the larger is this temperature increment. In other words, the highest limiting values λ_∞ and ion mobilities correspond to the smallest temperature coefficients.[2]

(2) The values of the temperature coefficient a of the viscosity run parallel with the viscosity itself. The greater the viscosity η, the larger is the temperature coefficient a:

$$\eta^{25}/a \sim 0.43.$$

(3) The temperature coefficient c of the maximal conductivity λ_∞ is practically identical with the temperature coefficient a of the viscosity in the same solvent or[3]

$$a \sim c$$

These new relationships were summarized by the rule: "Employing one and the same electrolyte, $N(C_2H_5)_4I$, in non-aqueous organic solvents, the *product of the internal friction and the limiting conductivity*, $\eta \cdot \lambda_\infty$, *is independent of the solvent and of the temperature.*"[4]

The $\lambda_\infty \cdot \eta = K$ rule was received like so many other new theoretical pronouncements. One group of scientists ultimately regarded it as a perfectly obvious generalization which had long been known, and linked it with Stokes' law. The other group discarded it as faulty and inadequate.

[1] See Lincoln, J. phys. chem., **3**, 457 (1899). This investigator considers the extrapolation of the maximal conductivities, λ_∞, possible only in methyl and ethyl alcohol. However, Walden was able to do so in all solvents employed by him. Lincoln also states that the conductivity decreases with temperature. Walden has conclusively proved the temperature coefficient to be normally postive. Only in cases where chemical decomposition or solvolysis of electrolytes takes place, is the temperature coefficient negative.

[2] Walden, Z. physik. Chem., **54**, 226 (1905).

[3] Walden, *ibid.*, **55**, 233, 247 (1906).

[4] *op. cit.*, **55**, 249 (1906).

It is to be assumed that the previously mentioned specialists (Jahn, Abegg, and others) knew of the Stokes law (1850) dealing with the slow stationary movement of a sphere in a liquid. Nevertheless, they stated that not even a theoretical relationship between the mobility of the ions and the properties of a medium could be predicted. Later, Stoke's law

$$K = \text{constant} = 6\pi \cdot \eta \cdot r \cdot v$$

(where v = velocity, η = viscosity, r = radius of the sphere) was repeatedly applied to ions and their mobility as dependent on viscosity.[1]

In particular by the comprehensive measurements of Dutoit and Duperthuis[2] using sodium iodide in ethyl, propyl, isobutyl and amyl alcohols, as well as acetone and pyridine, was the Walden rule $\lambda_\infty \cdot \eta = K$ shown to be apparently not verifiable. No constant for the product $\lambda_\infty \cdot \eta$ could be obtained either in one and the same solvent at different temperatures, or in various media at the same temperature (see Table XLIX).

TABLE XLIX

Products of Maximal Conductivities μ_∞ and viscosities η of Sodium Iodide in Various Solvents at Various Temperatures (μ_∞ in recipr. SIEMENS)

NaI		t = 0°	20°	40°	50°
Solvents:	C_2H_5OH	0.495	0.485	0.465	0.462
	C_4H_9OH	0.441	0.422	0.414	0.412
	$C_5H_{11}OH$	0.374	0.330	0.299	0.284
	Acetone	0.502	0.514	0.517	—
	Pyridine	0.573	0.567	0.564	0.564

However Walden[3] was able to show that these discrepancies disappeared almost entirely if the *maximal* con-

[1] Pellat, Compt. rend. **144**, 902 (1907); Hartley, Thomas and Applebey, J. Chem. Soc., **93**, 555 (1908); Einstein, Z. Elektrochem., **14**, 237 (1908); Lorenz, Z. physik. Chem., **73**, 252 (1910); Herzog, Z. Elektrochem., **16**, 1003 (1910).

[2] J. chim. phys., 699, 727 (1908).

[3] Z. physik. Chem., **78**, 257 (1911).

ductivities λ_∞ were evaluated uniformly, that is, extrapolated by the cube-root formula, $\lambda_\infty = \lambda_v + b\sqrt[3]{c}$. An average value

$$\mu_\infty \cdot \eta \sim 0.520 \sim \text{constant}$$

was obtained for a given solvent at different temperatures, and in general for all solvents.

Further experimental material was subsequently contributed both by Walden and by other investigators and is summarized in Walden's book "Leitvermögen der Lösungen," pt. 1, pages 120-150 (1924). However, it was not until the publication of Ulich's monograph "Über die Beweglichkeit der elektrolytischen Ionen" (Berlin, 1927) that an exhaustive theoretical presentation of this subject was made. A complete collection of all the experimental material also is given, all maximal conductivities being for the first time extrapolated uniformly in accordance with the square-root formula, $\lambda_\infty = \lambda_v + a\sqrt{c}$, an expression which received its theoretical significance by the fundamental investigations of Debye and Hückel.

Table L illustrates how the contradictory results of Dutoit and Duperthuis have been transformed, as a result of Ulich's recalculated values, into evidence in favor of the Walden rule.

It thus seems that the first requirement of the rule has been fulfilled, namely, that the product $\lambda_\infty \cdot \eta$ is constant for a given salt for *each* individual solvent over a wide temperature range. However, from this revised data it is evident that the second requisite—that $\lambda_\infty \cdot \eta$ be equal to a constant in all solvents—is only approximately true. The same conclusion may also be drawn from data on another typical salt composed of elementary ions.

Here again (Table LI) $\lambda_\infty \cdot \eta$ remain constant for a given medium at all temperatures, but differ for each individual solvent. Let us consider this latter fact by itself, especially in view of the data presented in Table LII.

The significance of this decided variation of the product $\lambda_\infty \cdot \eta$ now becomes more evident. The low $\lambda_\infty \cdot \eta$-values may be ascribed to an enlargement of ionic radii be-

TABLE L

Proof of the Walden Rule in Ethyl alcohol, Acetone and Pyridine. (Sodium iodide as solute)

	Ethyl alcohol			Acetone			Pyridine		
t	η	λ_∞	$\lambda_\infty \cdot \eta$	η	λ_∞	$\lambda_\infty \cdot \eta$	η	λ_∞	$\lambda_\infty \cdot \eta$
0°	0.01772	30.5	0.529	0.00401	139	0.557	0.0136	46.8	0.638
10°	0.0145	37.0	0.537	0.00356	158	0.561	0.0113	56.4	0.638
18°	0.01241	42.9	0.532	0.00329	172	0.566	—	—	—
20°	0.0119	44.4	0.529	0.00323	175	0.564	0.00958	66.4	0.637
25°	0.01087	48.2	0.524	0.00316	183	0.578	—	—	—
30°	0.00990	53.0	0.525	0.00293	194	0.568	0.00829	76.7	0.637
40°	0.00828	63.0	0.521	0.00268	213	0.570	0.00724	88.0	0.638
50°	0.00701	76.0	0.527	0.00256	—	—	0.00639	100	0.640
60°	0.00596	88	0.521	—	—	—	0.00569	111	0.630
		Average value	0.527			0.566			0.637

cause of solvation and formation of complexes, a theory which would seem justified and which would make the

TABLE LI

Proof of the Walden Rule in Ethyl Alcohol and in Nitromethane. (Potassium Iodide as solute)

	Ethyl alcohol			Nitromethane*		
t	λ_∞	$\lambda_\infty \cdot \eta$	t	η	λ_∞	$\lambda_\infty \cdot \eta$
0	31.8	0.564	0	0.00829 0.00844	91.4	0.76 0.77
18	45	0.56	—	——	——	——
25	50.9	0.553	25	0.00611 0.00631	124	0.76 0.77
35	60	0.54	—	——	——	——
40	——	——	40	0.00526	145	0.76
50	76	0.53	50	0.00450	167.5	0.75
60	96	0.57	—	——	——	——
70	——	——	70	0.00392	194	0.76
85	——	——	85	0.00343	218	0.75
	Averages	0.55				0.76

*Philip and Oakley, J. Chem. Soc., **125**, 1189 (1924).

TABLE LII

The Product $\lambda_\infty \cdot \eta$ for Potassium Iodide in Various Solvents at 25°

Solvent:	Alcohol	Acetone	Methyl alcohol	Furfurol	Aceto-phenone
η =	0.01096	0.003158	0.00546	0.0149	0.0162
λ_∞ =	50.9	185.6	114.85	43.10	39.8
$\lambda_\infty \cdot \eta$ =	0.560	0.586	0.627	0.642	0.644

Solvent:	Aceto-nitrile	Pryidine (20°)	Nitro-methane	Sulphur dioxide (0°)
η =	0.00345	0.00958	0.00611	0.00394
λ_∞ =	198.3	71.3	124	260–270
$\lambda_\infty \cdot \eta$ =	0.684	0.682	0.76	1.04

behavior in organic media up to the nitromethane, which has few addition reactions, appear more logical. "Inexplicable," however, are the large values in liquid sulphur

dioxide, which certainly belongs to the solutes as the solution of the iodide is yellow. It may further be mentioned that in liquid ammonia

$$\lambda_\infty \cdot \eta = 339 \times 0.00266 = 0.902 \ (t = -33.5^\circ)$$

and in water

$$\lambda_\infty \cdot \eta = 130.5 \times 0.01056 = 1.378 \ (t = 18^\circ).$$

It was therefore found necessary to determine experimentally whether deviations as large as those noted in the case of simply constituted salts, were also to be found in the case of differently compounded salts. Organic cations (alkylated ammonium bases) were therefore linked both with elementary anions to form salts such as the original normal salt $N(C_2H_5)_4I$, as well as with a complex organic anion. As early as 1913 Walden subjected the binary salts piperidine *picrate* and tri-amylammonium picrate, synthesized in accordance with these principles, to conductivity measurements.[1] He was able to show that salts composed of *large* organic cations and anions give similar $\lambda_\infty \cdot \eta$ products both in *aqueous solutions and in organic* media. These facts had an important directional influence upon further investigations.

The first confirmatory work was begun with aqueous solutions[2] followed by investigations on methyl and ethyl alcohol[3] in addition to further work in acetone.[4] Unpublished investigations by Walden and his co-workers include the solvents: antimony trichloride, urethane, ethylene dichloride, dichlorethylene and tetrachloroethane.

The results of several of these studies may be mentioned briefly. The following salts were investigated in aqueous solutions at the temperatures 0°, 18° and 100°:

KCl, KNO_3, $KClO_4$, $KClO_3$, $KBrO_3$ and KIO_3,
$NaCl$, $NaNO_3$
$CsNO_3$
$LiClO_4$, $Li \cdot OC_6H_2(NO_2)_3$ (picrate)
$N(C_2H_5)_4 \cdot OC_6H_2(NO_2)_3$

[1] Walden, Bull. acad. sci. St. Petersburg, 559 (1913).
[2] Walden and Ulich, Z. physik. Chem., **106**, 49 (1923).
[3] Walden, Ulich and Laun, *ibid.*, **114**, 275, 297 (1925).
[4] Walden, Ulich and Busch, *ibid.*, **123**, 429 (1926).

Only the lithium and tetra-ethylammonium picrates give a $\lambda_\infty \cdot \eta$-product which is constant with temperature. Potassium iodate also shows a strong tendency to yield a $\lambda_\infty \cdot \eta$-product which is constant with temperature.

TABLE LIII

Proof of the Walden Rule in Aqueous Solution

		Lithium picrate $N(C_2H_5)_4 \cdot OC_6H_2(NO_2)_3$				KCl	
t	η_{H_2O}	λ_∞	$\lambda_\infty \cdot \eta$	λ_∞	$\lambda_\infty \cdot \eta$	λ_∞	$\lambda_\infty \cdot \eta$
0°	0.01796	34.2	0.614	31.2	0.560	81.8	1.469
18°	0.01056	58.1	0.614	53.3	0.563	129.8	1.371
100°	0.00284	215.0	0.611	197	0.560	406.0	1.153

Potassium chloride, a typical salt, is introduced in the above table in contrast to the tetra-ethylammonium and lithium picrates; a gradual change in the numerical values of the $\lambda_\infty \cdot \eta$-product is definitely indicated. In general it may be said that this "variation" or decrease in $\lambda_\infty \cdot \eta$-values between 0° and 100° is greater, the larger the value of λ_∞, or the ion mobility. Table LIV depicts the behavior of various salts in methyl alcohol, ethyl alcohol, and acetone.

The following conclusions may be drawn from the data obtained in the case of methyl and ethyl alcohols over the temperature interval t = 0° to 56°.

(1) The product $\lambda_\infty \cdot \eta$ is not at all or only slightly dependent upon the temperature.

(2) The chemical constitution of the cations and anions exerts a very definite influence upon the size of the product. Salts with isomeric cations and identical anions have different values for the $\lambda_\infty \cdot \eta$-product.

(3) The nature of the ions influences the temperature constancy of the product $\lambda_\infty \cdot \eta$ so that it is constant in the case of salts with large organic ions—picrate and styphnate anions, tetra-ethylammonium cation—whereas the chlorides seem to reveal a slight progressive change.

A greater number of salts was investigated in *acetone*, and from the measurements it is indeed remarkable: (1) that

TABLE LIV

Conductivity Data in Methyl and Ethyl Alcohols and Acetone

Salt	t	λ^t_∞	η^t	$\lambda^t_\infty \cdot \eta^t$	Average
	Solvent: Methyl alcohol, $\epsilon_{25} = 30$ (32)				
Tetra-ethyl-	0	72.5	0.00792	0.574	
ammonium-	25	102.9	.00546	0.562	0.566
picrate	56	153.4	.00371	0.569	
Tetramethyl-	0	80.3	0.00792	0.636	
ammonium-	25	117	.00546	0.639	0.640
chloride	56	173.0	.00371	0.642	
Diethylamine-	0	74.0	0.00792	0.586	
hydrochloride	25	108.3	.00546	0.591	0.591
	56	159.6	.00371	0.592	
Isobutylamine-	0	67.0-67.2	0.00792	0.532	
hydrochloride	25	98.8	.00546	0.540	0.540
	56	146.4(-147.0)	.00371	0.543	
Tetra-ethyl-	0	82	0.00792	0.650	
ammonium-	25	120	.00546	0.655	0.652
styphnate	56	173	.00371	0.642	
	Solvent: Ethyl alcohol, $\epsilon_{25} = 24$				
Tetra-ethyl-	0	32.0	0.01773	0.567	
ammonium-	25	51.5	.01096	0.565	0.565
picrate	56	88.7	.006355	0.564	
Tetramethyl-	0	29.5-30.2	0.01773	(0.536)	
ammonium-	25	50.6	.01096	0.555	0.555
chloride	56	87.0-87.6	.006355	0.555	
Diethylamine-	0	28	0.01773	(0.497)	
hydrochloride	25	47.1	.01096	0.518	0.517
	56	81-83 (81.5)	.006355	0.516	
Isobutylamine-	0	24.0-24.4	0.01773	(0.433)	
hydrochloride	25	42.3	.01096	0.464	0.464
	56	73-74	.006355	0.464	
Tetra-ethyl-	0	34-39 (37)	0.01773	0.656	
ammonium-	25	58-62 (60)	.01096	0.658	0.655
styphnate	56	95-110 (103)	.006355	0.651	

TABLE LIV—continued

Conductivity Data in Methyl and Ethyl Alcohols and Acetone

Salt	$t =$ / $\eta =$	0° 0.003962	25° 0.003158	50° 0.002559	$\lambda_\infty \cdot \eta$ (average)
Solvent: Acetone, $\epsilon_{25} = 21$					
Tetra-ethylammonium picrate	$\lambda_\infty =$	141.4	177.3	218.6	
	$\lambda_\infty \cdot \eta =$	0.560	0.560	0.559	0.560
Tetra-ethylammonium styphnate	$\lambda_\infty =$	165	208	256	
	$\lambda_\infty \cdot \eta =$	0.652	0.657	0.655	0.655
Tetra-ethylammonium iodide	$\lambda_\infty =$	166.4	209.0	256.2	
	$\lambda_\infty \cdot \eta =$	0.660	0.660	0.656	0.659
Tetra-ethylammonium chloride	$\lambda_\infty =$	158.1	198.1	242.4	
	$\lambda_\infty \cdot \eta =$	0.626	0.626	0.620	0.624
Tetra-ethylammonium perchlorate	$\lambda_\infty =$	166.5	208.7	256.0	
	$\lambda \cdot \eta =$	0.660	0.659	0.655	0.658
Dinitrophenyl pyridinium picrate	$\lambda_\infty =$	120.5	151.5	186.5	
	$\lambda_\infty \cdot \eta =$	0.478	0.478	0.477	0.478
Tetramethylammonium picrate	$\lambda_\infty =$	148.7	187.0	229.4	
	$\lambda_\infty \cdot \eta =$	0.589	0.591	0.587	0.589
Isobutylammonium picrate	$\lambda_\infty =$	140.8	176.6	217.6	
	$\lambda_\infty \cdot \eta =$	0.558	0.558	0.557	0.558
Potassium iodide	$\lambda_\infty =$	147.8	185.6	229.2	
	$\lambda_\infty \cdot \eta =$	0.586	0.586	0.586	0.586
Sodium iodide	$\lambda_\infty =$	145.0	184.5	227.4	
	$\lambda_\infty \cdot \eta =$	0.575	0.582	0.581	0.579
Lithium picrate	$\lambda_\infty =$	123.6	155.0	191.0	
	$\lambda_\infty \cdot \eta =$	0.490	0.490	0.489	0.490
Barium perchlorate	$\lambda_\infty =$	160.9	201.2	248.2	
	$\lambda_\infty \cdot \eta =$	0.638	0.635	0.635	0.636

practically all salts yield a $\lambda_\infty \cdot \eta$-product which is constant with temperature; (2) that isomeric salts, such as $N(CH_3)_4^+$- and $N(C_4H_9)H_3^+$-picrates exhibit different values for this product; (3) that both binary (uni-univalent) and

ternary (tetra-ethylammonium styphnate and barium perchlorate) salts obey the rule, $\lambda_\infty \cdot \eta$ = constant.

The nature of the ions, be they elementary cations or anions or compound organic cations, and organic as well as inorganic anions such as the perchlorate ion, apparently exerts no influence on the temperature constancy of $\lambda_\infty \cdot \eta$ in acetone.

From among the salts which had been investigated the following were chosen for further study: first, those which had been found to give a product $\lambda_\infty \cdot \eta$ = constant with temperature in each individual solvent; secondly, those which had been found to have practically identical values for the product $\lambda_\infty \cdot \eta$ in many different solvents. These were the properties which were supposed from our general rule $\lambda_\infty \cdot \eta$ = constant, as based upon the behavior of normal salts. Table LV gives data for one such "ideal salt."

The average value 0.563 may be assumed to hold in water for all temperatures between 0° and 100°, as well as for the other chemically and physically varying solvents. It should be emphasized that the viscosity varies from η = 0.01796 to 0.00256 and the dielectric constant ϵ from 89 to 9.

Tetra-ethylammonium picrate apparently fulfills all requirements:

(1) It consists of two large organic ions: $N(C_2H_5)_4^+$ and $C_6H_2(NO_2)_3O^-$.

(2) As a typical strong binary salt (in water) it exhibits a temperature constancy for $\lambda^t_\infty \cdot \eta^t$ between t = 0° and 100° in water and between 0° and 50–56° in the non-aqueous solvents which were subjected to experiment.

(3) The numerical value of $\lambda_\infty \cdot \eta^t$ is constant for all investigated solvents at all temperatures employed.

This salt can therefore be looked upon as a "normal salt" in the sense of the rule

$$\lambda^t_\infty \cdot \eta^t = \text{constant.}$$

The product $\lambda_\infty \cdot \eta$ is actually independent of the temperature and of the solvent. Several other examples are appended in Tables LVI to LIX.

TABLE LV

Tetraethylammonium Picrate, $N(C_2H_5)_4^+ . [OC_6H_2(NO_2)_3]^-$

Solvent	t	λt_∞	η^t	$\lambda t_\infty . \eta^t$
Water	0	31.2[1]	0.01796[4]	0.560
	18	53.3[1]	0.01056	0.563
	100	197 [1]	0.00284	0.560
Methyl alcohol*	0	72.5[2]	0.00792	0.574
	25	102.9[2]	0.00546[5]	0.562
	56	153.4[2]	0.00371[6]	0.569
Ethyl alcohol	0	32.0[2]	0.01773[7]	0.567
	25	51.5[2]	0.01096	0.565
	56	88.7[2]	0.006355	0.564
Acetone	0	141.4[3]	0.003962[3]	0.560
	25	177.3[3]	0.003158[3]	0.560
	50	218.6[3]	0.002559[3]	0.559
Ethylene chloride	25	71.3	0.007853[8]	0.560
($C_2H_4Cl_2$)	0	49.4	0.011328	0.560
	50	95.2	0.005844	0.556

Average value 0.563

*The viscosities for methyl alcohol as given in the literature are not concordant. At $t = 0°$ Pagliani and Batelli find $\eta = 0.00734$, whereas Thorpe and Rodger give a value $\eta = 0.008166$.

[1] Walden and Ulich, Z. physik. Chem., **106**, 77 (1923)
[2] Walden, Ulich and Laun, *ibid.*, **114**, 295 (1924).
[3] Walden, Ulich and Busch, *ibid.*, **123**, 452 (1926).
[4] Bingham and White, Bur. Standards, Sci. Papers, No. 298 (1917).
[5] Lewis, J. Am. Chem. Soc., **47**, 626 (1925).
[6] Völlmer, 1894.
[7] Bingham and Jackson, Bur. Standards, Sci. Papers, No. 298 (1917).
[8] Unpublished investigations.

TABLE LVI

Tetramethylammonium Picrate $N(CH_3)_4 \cdot OC_6H_2(NO_2)_3$

Solvent:	t	λt_∞	η^t	$\lambda t_\infty . \eta^t$
Acetone	0	148.7	0.003962	0.589
	25	187.0	.003158	0.591
	50	229.4	.002559	0.587

The product $\lambda^t{}_\infty \cdot \eta^t$ is constant with temperature but varies with the solvent.

TABLE LVII

Tetrapropylammonium Picrate $N(C_3H_7)_4 \cdot OC_6H_2(NO_2)_3$

Solvents:	t	λt_∞	η^t	$\lambda t_\infty \cdot \eta^t$
Water	18	46.0	0.01056	0.486
Acetone	25	156.6	0.003158	0.494
Ethylene chloride	25	62.1	0.007853	0.488
Dichlorethylene	25	113.2	0.004365	0.494
Tetrachloraethane	25	30.3	0.01612	0.488
			Average	0.490

TABLE LVIII

Tetra-isoamylammonium Picrate $N(C_5H_{11})_4 \cdot OC_6H_2(NO_2)_3$

Ethylene chloride		λ_∞	η	$\lambda_\infty \cdot \eta$
$C_2H_4Cl_2$	t = 25°	54.0	0.007853	0.424

TABLE LIX

Tetra-ethylammonium Styphnate

$$\tfrac{1}{2}\left[(C_2H_5)_4N \diagdown O \diagup C_6H(NO_2)_3 \diagdown O \diagup N(C_2H_5)_4\right]$$

Solvent:	t	λt_∞	$\lambda t_\infty \cdot \eta^t$
Methyl alcohol	0	82	0.650
	25	120	0.655
	56	173	0.649
Ethyl alcohol	0	37	0.656
	25	60	0.658
	56	103	0.651
Acetone	0	165	0.652
	25	208	0.657
	50	256	0.655
		Average	0.654

Tetrapropylammonium picrate and tetra-ethylammonium styphnate are worthy of special attention. The first of these two salts had been studied previously both in the so-called

"non-conductors," $C_2H_4Cl_2$, $C_2H_2Cl_2$ (cis-) and $C_2H_2Cl_4$, as well as in water and in acetone. The product $\lambda^t_\infty \cdot \eta^t$ is constant with temperature in all of these solvents. Tetraethyl styphnate deserves special consideration because it is a *ternary* salt and even as such follows the $\lambda_\infty \cdot \eta$ = constant rule. Its value 0.654 is independent both of the temperature and of the nature of the solvent.

(C) RELATIONSHIP BETWEEN THE SIZE OF $\lambda_\infty \cdot \eta$ AND THE COMPOSITION

Herzog[1] derived the equation

$$\lambda_\infty \cdot \eta_\infty = \frac{1.042 \times 10^{-4}}{\sqrt[3]{V_m}} \quad \text{or} \quad \lambda_\infty \cdot \eta_\infty \sqrt[3]{V_m} = K$$

for the Walden rule from the Stokes-Einstein Law.

The usefulness of this relationship can be tested by applying it to the $\lambda_\infty \cdot \eta$-values previously determined for non- or slightly solvated picrates.

TABLE LX

Herzog's Equation applied to $\lambda_\infty \cdot \eta$ for Picrates

Salts	Mol. wt. M	Density $d_{sol.}$	$V_m = M/d$	$\lambda_\infty \eta$	$\lambda_\infty \cdot \eta \sqrt[3]{V_m}$	$\lambda_\infty \cdot \eta \sqrt{M}$
$\overset{+}{N}(CH_3)_4 \cdot \overset{-}{O}C_6H_2(NO_2)_3$	302.14	1.42	212.8	0.589	3.52	10.24
$\overset{+}{N}(C_2H_5)_4 \cdot \overset{-}{O}C_6H_2(NO_2)_3$	358.21	1.4	255.9	0.563	3.57	10.65
$\overset{+}{N}(C_3H_7)_4 \cdot \overset{-}{O}C_6H_2(NO_2)_3$	414.27	1.22	339.2	0.490	3.42	10.05
iso-$\overset{+}{N}(C_5H_{11}) \cdot \overset{-}{O}C_6H_2(NO_2)_3$	526.4	1.1	478.5	0.424	3.32	9.73
				Average	3.46	10.17
For acetone solutions of:						
Dinitrophenyl pyridinium picrate	474.1	1.08	439.0	0.478	3.63	10.41
Di-ethylammonium picrate	302.14	1.4	215.8	0.555	3.33	9.64
Isobutylammonium picrate	302.14	1.45	208.4	0.558	3.31	9.70
				Average	3.42	10
Lithium picrate	235.0	1.7	138.1	0.490	2.53	7.51

[1] Z. Elektrochem., 16, 1003 (1910).

This summary brings together the numerical data for seven picrates of organic bases, that is, for salts composed of large organic ions. The next to last column contains the calculated values of $\lambda_\infty \cdot \eta \cdot \sqrt[3]{V_m}$. An approximate constancy is obtained here as the average value is about 3.42. The last column contains numerical data calculated on the basis of another relationship, derived empirically by Walden,[1] which requires that $\lambda_\infty \cdot \eta \cdot \sqrt{M} \sim$ constant. Here also the individual values lie in the neighborhood of 10, that is,

$$\lambda_\infty \cdot \eta \cdot \sqrt{M} \sim \text{constant} \sim 10$$

where M equals the molar weight of the corresponding salt (M = 302.14 to 526.4)

Degree of Solvation.

Even though the seven picrates of the ammonium bases show a satisfactory agreement with both rules, lithium picrate, a salt containing a small elementary cation, distinguishes itself by its divergent behavior. The product $\lambda_\infty \cdot \eta \cdot \sqrt[3]{V_m}$ is much too small as compared with the average value 3.42. Likewise, $\lambda_\infty \cdot \eta \cdot \sqrt{M} = 7.51$ is far below the average value, 10, of the other picrates. What is the cause of its unique position? According to the Herzog equation all salts of a similar type should possess the same constant K in the same medium. Conversely, where the product $\lambda_\infty \cdot \eta \sqrt[3]{V_m}$ for a salt possesses a divergent value, one may conclude that the ionic radius has been changed by solvation. On the basis of this assumption an approximate calculation of the degree of solvation of the degree of solvation may be made. Let

$$\sqrt[3]{V_m} = \sqrt[3]{V_{(\text{salt} + \text{solv.})}} = K/\eta \cdot \lambda_\infty$$

or in acetone

$$V_m = (3.42/\eta \cdot \lambda_\infty)^3$$

(1) For lithium picrate $V_m = (3.42/0.490)^3 = 340$. Subtraction of its own volume V = 138.1 gives

$$(340 - 138.1) = 201.9,$$

[1] Z. Elektrochem., **12**, 77 (1906).

which represents the volume of the acetone as a solvate shell. Recalculation in terms of weight and number of mols, where $V = \frac{M_{acetone}}{d_{acetone}} = \frac{58}{0.785} = 73.9$

gives $x = \frac{201.9}{V} = 2.74$ mols acetone.

In a similar manner the formula $\lambda_\infty \cdot \eta \cdot \sqrt{M} \sim 10$ leads through $\sqrt{M} = \frac{10}{\lambda_\infty \cdot \eta} = \frac{10}{0.490}$, or $M = (20.4)^2 = 416$, to a value

$$x = \frac{(416 - 235)}{58(CH_3COCH_3)} = 3.1 \text{ mols acetone as a shell}$$

enveloping lithium picrate. Since the picrate ion is regarded as a non-solvated ion it is assumed that three mols of acetone are linked with the lithium ion.

The degree of solvation in acetone of the sodium and potassium ions in combination with the picrates may be determined in the same way. The mobilities as calculated in acetone are used for this purpose.

(2) Sodium picrate: $l_K + l_A = 68.6 + 84.5 = 153.1 = \lambda_\infty$, and when $\eta = 0.003158$, then $\lambda_\infty \cdot \eta = 153.1 \times 0.03158 = 0.483$. $M = 251$, and by $\lambda_\infty \cdot \eta \cdot \sqrt{M} \sim 10$,

$$x = \frac{428.6 - 251}{58} = 3.0 \text{ mols acetone with each } Na^+ \text{ ion.}$$

(3) Potassium picrate, $M = 267$; $\lambda_\infty = 69.6 + 84.5 = 154.1$ then

$$\lambda_\infty \cdot \eta = 154.1 \times 0.003158 = 0.487$$

and $x = \frac{421.6 - 267}{58} = \frac{154.6}{58} = 2.6$ mols acetone with each potassium ion.

The degree of solvation in acetone is, then, in the order $Li^+ \geqq Na^+ > K^+$. If the large organic picrate ion is assumed to be non-solvated, then the extent of solvation is

analogous for the cations :	Li^+	Na^+	K^+
mols acetone :	$\leqq 3$	3	$\leqq 3$

(D) ION MOBILITIES l AND VISCOSITY η

On the basis of the observational material presented above we may assume that certain binary and ternary salts composed of large organic ions, follow the general rule

$$\lambda_\infty \cdot \eta = K$$

i.e. in these salts the product of the maximal conductivity, λ_∞, of the salt and the viscosity, η, of the solvent is independent of the temperature and nature of the solvent (Walden, 1906). Further considerations lead us to conclude that a similar relationship may be adduced and experimentally proven for the ions themselves; that the product of the ion mobilities l_A and l_K (cation and anion) and the viscosity η, is also independent of the temperature and the nature of the solvent. The maximal conductivity in all solvents and of all electrolytes is equal to the sum of the ion mobilities (Kohlrausch's Law):

$$\lambda_\infty = (l_K + l_A).$$

If the rule $\lambda_\infty \cdot \eta = K$ (constant) is valid for the maximal conductivities, there is no reason why the following equations should not hold also:[1]

$$\lambda_\infty \cdot \eta = (l_K + l_A)\eta = K, \text{ and}$$

$$l_K\eta = K_1 \text{ and } l_A \cdot \eta = K_2,$$

and $$(l_K + l_A)\eta = (K_1 + K_2) = K.$$

To illustrate this relationship we may again make use of our normal salt, tetra-ethylammonium picrate. Let us start with the measurements in water at 18°. The data for potassium picrate may also be employed under similar conditions. Since the mobility of the potassium ion at 18°

[1] Walden, Z. anorg. Chem., 113, 113 (1920).

is known with sufficient accuracy, one can readily determine the mobility of the picrate ion from the maximal conductivity of potassium picrate. That determination and the limiting conductivity λ_∞ of tetra-ethylammonium picrate bring us the mobility of the $N(C_2H_5)_4^+$ ion itself.

The mobility of the potassium ion at 18° at infinite dilution in aqueous solution, $l_K^{18} = 64.5$.[1] The following calculations may then be made from Walden's data.[2]

I. Potassium picrate $\lambda_\infty^{18} = 89.6 \pm 0.3$
Potassium ion $l_K^{18} - 64.5$
Picrate ion $Pi^- = 25.1 (\pm 0.3)$
assumed for Pi^- **25.3**

II. Tetra-ethylammonium picrate $\lambda_\infty^{18} = 53.2 \pm 0.2$
minus picrate ion Pi^- at 18° $- 25.3$
$\therefore$ found for $N(C_2H_5)_4^+$ at 18° 28.0

Thus the product

$l_{Pi}^{18} \cdot \eta_{H_2O}^{18} = 25.3 \times 0.01056 = 0.267 =$ picrate ion

and $l_{N(C_2H_5)_4}^{18} \cdot \eta_{H_2O}^{18} = 28.0 \times 0.01056 = 0.296 =$ tetra-ethylammonium ion

or $\lambda_\infty^{18} \cdot \eta^{18} = (l_{Pi}^{18} + l_{N(C_2H_5)_4}^{18}) = (0.267 + 0.296) = 0.563$*

Calculated for the temperature t = 25°, in water

$$l_{Pi}^{25} = l_{Pi}^{18} \times \frac{\eta^{18}}{\eta^{25}} = 25.3 \times \frac{0.01056}{0.008941} = 29.9, \text{ picrate ion,}$$

$$\text{and } N(C_2H_5)_4\text{-ion} = 28.0 \times \frac{0.01056}{0.008941} = 33.1,$$

or $N(C_2H_5)_4$-picrate $(29.9 + 33.1) = 63.0 = \lambda_\infty^{25}$.

The *picrate ion* may be taken as the *basis for further considerations* since

$$l_{Pi}^t \times \eta^t = 0.267$$

[1] *See* Landolt-Börnstein's Tabellen. Ergzgs.-Bd. I, 620 (1927).
[2] Walden and Ulich, Z. physik. Chem., **106**, 77 (1923).
* This value is identical with the average value previously determined experimentally

a value constant for all temperatures and in any ionizing solvent. The mobility of the picrate ion may generally be calculated from the equation

$$l_{Pi}{}^{t} = 0.267/\eta^{t}, \text{ where } \eta^{t} = \text{viscosity at } t°.$$

TABLE LXI

Calculation of Ion Mobilities in Various Solvents

	$t =$	0°	25°	50°	100°
a) in Water:	η^{t}	= 0.01796	0.008941	0.005497	0.00282
Picrate ion: $0.267/\eta^{t}$		= 14.87	29.9	48.6	94.6
$N(C_2H_5)_4$ ion: $0.296/\eta^{t}$		= 16.48	33.1	53.8	104.9
$\lambda_{\infty\,calc} = l_{Pi} + l_{N(C_2H_5)_4}$		= 31.35	63.0	102.4	199.5
	$\lambda_{\infty\,obs}$	= 31.2±0.2	63.0		195.6±1.0*
b) in Methyl alcohol	η^{t}	= 0.00792	.00546	.00403	
Picrate ion:	l_{Pi}	= 33.7	48.9	66.3	
c) in Ethyl alcohol	η^{t}	= 0.01773	0.01096	.00702	
Picrate ion:	l_{Pi}	= 15.1	24.4	38.0	
$l_{N(C_2H_5)_4} = 0.296/\eta^{t}$		= 16.7	27.0	42.2	
	$\lambda_{\infty\,calc}$	= 31.8	51.4	80.2	
	$\lambda_{\infty\,obs}$	= 32.0	51.5		
d) in Acetone,	η^{t}	= 0.003962	.003158	.002559	
Picrate ion	l_{Pi}	= 67.4	84.5	104.3	
e) in Ethylene chloride	η^{t}	= 0.01133	0.00785	0.005844	
Picrate ion l_{Pi} $0.267/\eta^{t}$		= 23.5	33.9	45.7	
$l_{N(C_2H_5)_4}{}^{+} = 0.296/\eta^{t}$		= 26.1	37.7	50.6	
	$\lambda_{\infty\,calc}$	= 49.6	71.6	96.3	
	$\lambda_{\infty\,obs}$	= 49.4	71.3	95.2	

* Z. physik. Chem., 106, 97 (1923).

Let us now consider several examples of salts in which the $\lambda_{\infty} \cdot \eta$-product is constant with temperature in each individual solvent only, whereas the numerical value of

TABLE LXII
Ion Mobilities in Methyl Alcohol

	t = 0°	25°	50°
Tetramethylammonium chloride $N(CH_3)_4Cl$			
Cl^--ion: l_{Cl} =	35.4	51.3	75.5
temp.-const. ηl_{Cl} =	0.280	0.280	0.280
$N(CH_3)_4^+$-ion:			
temp.-const. $\eta . l_{N(CH_3)_4}$ =	0.359	0.359	0.359
$l_{N(CH_3)_4}$ =	45.3	65.8	96.8
$\lambda_{\infty\,calc} = l_{Cl} + l_{N(CH_3)_4}$ =	80.7	117.1	172.3
$\lambda_{\infty\,obs}$ =	80.3	117.0	173.0
Diethylammonium chloride $N(C_2H_5)_2H_2Cl$	Cl-ion as above: $l_{Cl} \cdot \eta$ = 0.280. Then $N(C_2H_5)_2H_2^+$-ion l_K = 0.311 (= 0.591 − 0.280).		
Then $N(C_2H_5)_2H_2^+$, mobility $l_{N(C_2H_5)_2H_2}$ =	39.2	57.0	83.8
$\lambda_{\infty\,calc} = l_{Cl} + l_{N(C_2H_5)_2H_2}$ =	74.6	108.3	159.3
$\lambda_{\infty\,obs}$ =	74.0	108.3	159.6

TABLE LXIII
Ion Mobilities in Acetone

	t = 0°	25°	50°
Sodium iodide, NaI:			
Iodide-ion l_I =	92.7	116.2	143.4
Taken as constant with temp. $l_I \cdot \eta$ =	0.367	0.367	0.367
Na^+-ion l_{Na} =	52.5	68.3	84.0
$l_{Na} \cdot \eta$ =	0.208	0.216	0.215
Potassium iodide, KI:			
K^+-ion l_K =	55.1	69.4	85.8
$l_K \cdot \eta$ =	0.218	0.219	0.219
$\lambda_{\infty\,calc} = l_K + l_I$ =	147.8	185.6	229.2
$\lambda_{\infty\,obs}$ =	147.8	185.6	229.2

$\lambda_\infty \cdot \eta$ changes when the solvent is varied. The chlorides of the ammonium bases and the iodides of the alkali metals belong to this class.

It was found that the product $\lambda_\infty \cdot \eta$ is constant regardless of temperature and solvent in the case of those salts composed of large organic ions. Let us determine for several such examples in what form this constancy is expressed in the ions (or mobilities) themselves, that is, within what limits the product $l \cdot \eta$ varies from one solvent to the next.

TABLE LXIV

A. The Cation $N(C_2H_5)_4^+$ *at Various Temperatures and in Different Media.*

(Average value $\lambda_\infty{}^t \cdot \eta^t = 0.563$; picrate ion $l_{Pi}{}^t \eta^t = 0.267 = K$)
Ion $N(C_2H_5)_4^+ = 0.296$.

Solvent	t°	Mobility of $N(C_2H_5)_4^+$	$\eta l_{N(C_2H_5)_4}$
Water	0	16.3	0.293
	18	28.0	0.296
	100	103.2	0.293
Methyl alcohol	0	38.7	0.307?
	25	54.0	0.295
	56	81.4	0.302
Ethyl alcohol	0	16.9	0.300
	25	27.2	0.298
	56	46.7	0.297
Acetone	0	73.4	0.293
	25	92.8	0.293
	50	114.1	0.292
Ethylene chloride	0	25.9	0.293
	25	37.3	0.293
	50	49.5	0.289
			Average 0.296

TABLE LXIV—*concluded*

B. Cation $N(C_3H_7)_4^+$; $l_K \cdot \eta = 0.223$

Solvent	t°	Mobility of $N(C_3H_7)_4^+$	$l_K \cdot \eta$
Water	18	20.7	0.219
Acetone	25	71.9	0.227
Ethylene chloride	25	28.1	0.221
Dichlorethylene	25	52.0	0.227
Tetrachloroethane	25	13.7	0.221
Propionitrile	25	56	0.23
Nitrobenzene	25	11.6	(0.212)
Epichlorhydrine	25	21.5	0.221

Average 0.223

C. Styphnate Anion $\frac{1}{2}\left[C_6H(NO_2)_3\begin{matrix}O^{-}\\O^{-}\end{matrix}\right]$

$\eta\lambda_\infty - \eta l_{N(C_2H_5)_4} = 0.654 - 0.296 = 0.358$

Calcd. from average of the picrate ion.

Solvent	t°	Ion Mobility of styphnate	Found $\eta l_{St.}$
Methyl alcohol	0	44.7	0.354
	25	65.8	0.359
	56	95.2	0.353
Ethyl alcohol	0	20.3	0.360
	25	33.0	0.362
	56	55.9	0.355
Acetone	0	89.9	0.356
	25	114.3	0.361
	50	140.3	0.359

Average 0.358

(E) CALCULATION OF ION MOBILITIES FROM λ_∞ IN NON-AQUEOUS SOLVENTS

(Calculation of transference numbers.)

In view of the practically limitless number of solvents and the large number of electrolytes to be investigated, the problem of ion mobilities in non-aqueous solvents represents a field of research of simply tremendous proportions.

The experimental solution of this problem has held the attention of many outstanding electrochemists. Nevertheless it must be said that the results attained are not commensurate with the energy expended. Two obstacles may have contributed to this effect. One trouble lay in the fact that up until very recently the method for determination of the maximal conductivity, λ_∞, was still theoretically and experimentally disputed and unsettled. Its certified determination was absolutely necessary since the individual mobilities l_A and l_K were derived by the equation

$$\lambda_\infty = l_{\text{cation}} + l_{\text{anion}} = l_K + l_A$$

Experimentally a still greater obstacle is connected with the determination of the transference numbers n_K and n_A. According to the classic dissociation theory

$$n_K = l_K/(l_K + l_A) = l_K/\lambda_\infty = \text{constant},$$

or $$n_A = l_A/\lambda_\infty = \text{constant}.$$

The determination of the mobility l of the individual ions, in accordance with this procedure, presupposes a knowledge of the transference number n. Experience has shown that particularly in non-aqueous solvents at moderate dilutions transference numbers are not constant, but quite variable. To obtain a constant value the investigations must be carried out at great dilutions, that is at dilutions where complex molecules and complex ions do not occur. All possibility of stepwise dissociation and intermediate ion formation must be precluded. To illustrate this factor in the case of a typical salt Schlundt's measurements (1902) of silver nitrate in acetonitrile are selected.

$t \sim 18°$	$v =$ 1	4.0	10	35
anion n_{NO_3}	= 0.617	0.578	0.552	0.527

Table LXV gives a summary of the ion mobilities in ethyl alcohol and demonstrates how both λ_∞ and n may act together and—according to the personal equation of each investigator—influence the mobility values of even very simple ions.

The method, followed since 1920 by Walden, with which it was hoped eventually to obtain further elucida-

TABLE LXV
Ion Mobilities in Ethyl Alcohol

Ions	H^+	$N(C_2H_5)_4^+$	Na^+	K^+	Li^+	Cl^-	I^-	Picrate	Authority
Ion Mobilities l (18°)	32.1	—	14.5	21.5	10.4	23.8	27.5	—	Godlewski 1904; Högglund 1912.
(25°)	38.5	—	—	—	—	—	—	10.5	Bredig, Braune, 1911.
(25°)	56	—	13.1	—	—	33.4	—	37	H. Goldschmidt, 1915.
(18°)	—	—	20.3	20.4	16.8	—	21.5	—	Walden (1923) from Dutoit's measurements
(25°)	62.9	31	19.8	27.5	—	28	28.8	27	Walden (1920)
(25°)	62	28	21.5	25.8	17.5	25–27	27.2	27	Walden (1924)
(25°)	62.8	27.1	22.3	24.5	17.8	21.2	26.4	24.4	Walden (1927)

tion of this question, makes use of the limiting values λ_∞ extrapolated by means of the cube-root formula and rests upon two fundamental premises; first: application of the rule $\lambda_\infty \cdot \eta = \text{constant}$, to the ion mobilities themselves

$$\lambda_\infty \cdot \eta = (l_K + l_A)\eta = l_K \cdot \eta + l_A \cdot \eta = K,$$

or $$l_K \eta = K_1 \text{ and } l_A \cdot \eta = K_2,$$

and $$(l_K \cdot \eta + l_A \cdot \eta) = (K_1 + K_2) = K^1$$

Secondly: ever since Völlmer's investigations (1894) it has been regarded as an established rule that the relationship between the maximal conductivities in water and in alcohol, at 18°, is practically a constant ratio. Thus,

$$\frac{\lambda_\infty \text{ in } C_2H_5OH}{\lambda_\infty \text{ in } H_2O} = 0.34 = \text{constant}$$

Völlmer also found the following relationship to exist between methyl alcohol and water:

$$\frac{\lambda_\infty \text{ in } CH_3OH}{\lambda_\infty \text{ in } H_2O} = 0.73 = \text{constant.}$$

Laszczynski (1895) established the following ratio between acetone and water

$$\frac{\lambda_\infty \text{ in acetone}}{\lambda_\infty \text{ in water}} = 1.32 \; (t = 18°)$$

Walden[2] was able to show that these widely used rules are not applicable generally, since each of his three classes of binary salts has a characteristic constant of its own. Thus for the ratio

$$\frac{\lambda_\infty \text{ in } C_2H_5OH}{\lambda_\infty \text{ in } H_2O}:$$

I—Salts with simple elementary ions, 0.35 (cf. Völlmer)
II—Salts with mixed ions, that is, those composed of one large organic ion and an elementary one, 0.511
III—Binary salts with large organic ions, 0.772

[1] Walden, Z. anorg. Chem., 113, 113 (1920).
[2] *Elektrochemie nichtwässeriger Lösungen*, p. 182 ff. (1923-1924).

Walden made the following statement regarding these facts: "Both the supporters and the opponents of the solvation theory agree that large organic ions are non-solvated. Investigations of combinations of such ions, accordingly, would be most liable to lead to simple relationships between ion mobility and viscosity of the solvent. The empirical ratio

$$\frac{\lambda_\infty \text{ in } C_2H_5OH}{\lambda_\infty \text{ in } H_2O} = 0.772$$

applies to ions of this kind. Numerically, the same ratio also expresses the viscosities of the two solvents at 25°, viz.,

$$\frac{0.00891}{0.01159} = 0.778.''$$

Walden subsequently extended these considerations to methyl alcohol, acetone, and others, and attempted to determine the individual ion mobilities given in Table LXV, next to the last line, more accurately on this basis.[1] For several reasons the ion mobilities thus determined left much to be desired in view of the fact (1) that the maximal conductivity data were of varied accuracy, since the limiting values were not uniformly extrapolated, and (2) because the number or kind of suitable electrolytes with large organic ions was insufficient.

To fill up these loop holes experimentally it was necessary to carry out precise determinations employing a uniform method of measurement and specially chosen or synthesized electrolytes. Tetra-ethylammonium picrate, $\overset{+}{N}(C_2H_5)_4 \cdot \bar{O}C_5H_2(NO_2)_3$ was chosen as the most satisfactory normal salt.

With the coöperation of several younger but experienced co-workers, a pretentious series of investigations was begun, some of the results of which have already been published, namely those

(1) In water at 0°, 18° or 100°[2]

[1] Walden, *Das Leitvermögen der Lösungen*, Pt. 1. p. 352 (1924).

[2] Walden and Ulich, Z. physik. Chem., **106**, 49 (1923); **107**, 219 (1923).

(2) In methyl alcohol and ethyl alcohol at 0°, 25° and 56°[1]
(3) In acetone at 0°, 25°, 50°[2]
A critical investigation "concerning the mobility of electrolytic ions" was made later by H. Ulich.[3]

In the next few pages we shall present the calculations for determining the ionic velocities, l, of the frequently employed monovalent ions.

IONIC VELOCITIES

I. *In Water*, t = 18°

The following data have been obtained previously (p. 302):

$t = 18°$, Picrate ion, $l_A^{18} = 25.3$,

$$\text{therefore } l_A \times \eta = 25.3 \times 0.01056 = 0.267$$

Tetra-ethylammonium ion $l_K^{18} = 28.0$,

$$\text{therefore } l_K \times \eta = 280 \times 0.01056 = 0.296$$

Converting to t = 25°:

$$\text{Picrate ion, } l_{Pi}^{25} = l_A^{18} \times \frac{\eta^{18}}{\eta^{25}} = 25.3 \times \frac{0.01056}{0.008941} = 29.9$$

$$N(C_2H_5)_4^+ \text{ ion: } l_K^{25} = l_K^{18} \times \frac{\eta^{18}}{\eta^{25}} = 28.0 \times \frac{0.01056}{0.008941} = 33.1$$

The researches of Bencowitz and Renshaw[4] offer material data for verifying these results. These investigators found the limiting conductivity of tetra-ethylammonium chloride to be $\lambda_\infty = 109.19$. If we assume the mobility of the chloride ion[5] as 76.3 then the cation

$$l_{N(C_2H_5)_4^+} = \lambda_{N(C_2H_5)_4Cl^-} - l_{Cl^-} = 109.19 - 76.3 = 32.9$$

The other λ_∞-value, calculated by the $\sqrt{C}$-formula and given by Bencowitz and Renshaw, is $\lambda_\infty = 109.73$. From it we obtain $N(C_2H_5)_4^+ = 109.73 - 76.3 = 33.43$.

[1] Walden, Ulich and Laun, *ibid.*, **114**, 275 (1924). Walden and Ulich, *ibid.*, **114**, 297 (1924).
[2] Walden, Ulich and Busch, *ibid.*, **132**, 429 (1926).
[3] *Ueber die Beweglichkeit der elektrolytischen Ionen.* 56 p. (Berlin, 1926).
[4] J. Am. Chem. Soc., **48**, 2152 (1926).
[5] Landolt-Börnstein's Tabellen. Supplementary Volume I, p. 620 (1927).

Depending upon the method used for extrapolating the maximal conductivity λ_∞, the average ion mobility value for the $N(C_2H_5)_4^+$ cation is

$$l_{N(C_2H_5)_4^+} = (32.9 \text{ to } 33.43) = 33.16,$$

which is in good agreement with the standard value, 33.1, given above.

This fundamental value can also be supported by the older data for tetra-ethylammonium chloride (Bredig) and the iodide (Philip and Courtman, H. C. Jones, and others), from which the maximal conductivities have been obtained using the $\sqrt{c}$-formula, viz.:

$N(C_2H_5)_4Cl$: $\lambda_\infty = 109.5$ and $l_{Cl} = 76.3$,

hence $l_{N(C_2H_5)_4^+} = 109.5 - 76.3 = 33.2$

$N(C_2H_5)_4I$: $\lambda_\infty = 109.7$ and $l_{I^-} = 76.7$,

hence $l_{N(C_2H_5)_4^+} = 109.7 - 76.7 = 33.0$.

The mean of both results is $l_{N(C_2H_5)_4^+} = 33.1$

II. *In Methyl Alcohol*, t = 25°.

Given: Tetra-ethylammonium picrate: $\lambda_\infty^{25} = 102.9$ (Walden, Ulich and Laun)

Sodium picrate $\lambda_\infty^{25} = 95$ (extrapolated from Goldschmidt's measurements).

For the picrate ion as standard $l_{Pi} \cdot \eta = 0.267$

where $\eta^{25}_{CH_3OH} = 0.00546$, and $l_{Pi} = \dfrac{0.267}{0.00546} = 48.9$

For the $N(C_2H_5)_4^+$ cation it follows

$$l_{N(C_2H_5)_4} = 102.9 - 48.9 = 54.0 \left(\text{or } \frac{0.296}{0.00546} = 54.1\right)$$

Sodium ion Na^+ . . . . $(95 - 48.9) = 46.1$ or about 46.[1]

Using the very accurate λ_∞^{25}-values of Frazer and Hartley for comparison we obtain Table LXVI:

[1] H. Frazer gives the value 45.7.

TABLE XLVI

									Ion mobilities:			Frazer and Hartley
from NaCl	λ_∞^{25}	=	96.95	(subtract	Na^+	= 46)	:	Chloride ion	=	50.95 (51)		51.3
" NaBr	"	=	101.5	("	Na^+	= 46)	:	Bromide "	=	55.5		55.5
" KBr	"	=	109.4	("	Br^-	= 55.5)	:	Potassium ion	=	53.9		53.8
" KI	"	=	114.9	("	K^+	= 53.9)	:	Iodide ion	=	61.0		61.0
" LiCl	"	=	90.9	("	Cl^-	= 51)	:	Lithium"	=	39.9		39.6
" $NaNO_3$	"	=	106.45	("	Na^+	= 46)	:	NO_3^- "	=	60.45	60.6	60.8
" KNO_3	"	=	114.55	("	K^+	= 53.9)	:	NO_3^- "	=	60.65		
" $AgNO_3$	"	=	112.95	("	NO_3^-	= 60.6)	:	Ag^+ "	=	52.35		52.2
" HCl	"	=	193.5	("	Cl^-	= 51.0)	:	H^+ "	=	142.5		142.2

from $N(CH_3)_4Cl$	λ_∞^{25}	=	117	(subtract	Cl^-	= 51.0)	:	$N(CH_3)_4^+$ ion	= 66.0	65.5 (as compared with 65.8, Table LXII).
" $N(CH_3)_4I$	"	=	126	("	I^-	= 61.0)	:	" "	= 65.0	
" $N(CH_3)_4NO_3$	"	=	126	("	NO_3^-	= 60.6)	:	" "	= 65.4	

In order to judge the results of Table LXVI, it is necessary to realize the wholly different points of departure of the two groups of investigators.

(1) Hartley and Frazer start with the experimentally determined transference number n_H of hydrogen chloride in methyl alcohol, using $n_H = 0.735$ for hydrogen ion and $\lambda_\infty = 193.5$ for HCl.

(2) Walden's procedure is based upon $l_{Pi} \cdot \eta = 0.267$ for the picrate ion, a figure which has been experimentally determined and assumed to be constant for all solvents.

Since both methods lead to identical mobilities for the individual ions they are mutually supporting and confirm the Walden rule $l \times \eta =$ constant which is the fundamental assumption.

If the above ion mobilities be employed in calculating the transference number of the much-studied silver nitrate, we obtain, as limiting value for the silver ion

$$n_{Ag} = \frac{52.4}{112.95} = 0.464 \text{ or } \frac{52.2}{112.95} = 0.462$$

Experimentally H. C. Jones, Bassett and Rouiller have found $n_{Ag} = 0.428$, whereas Gibbons and Getman find $n_{Ag} = 0.421$ to 0.465.

For lithium iodide the above data give for the iodide anion

$$n_I = 61/100.9 = 0.605$$

By direct measurement Carrara obtained $n_I = 0.621$ at $v = 45$.

For sodium iodide $n_{I(Calc.)} = 61/107 = 0.570$.

Table LXVII shows the extent of agreement between the maximal conductivities, λ_∞, as calculated from the ion mobilities $\lambda_\infty = l_K + l_A$ given above, and those determined directly by Hartley and Frazer.[1]

[1] Proc. Roy. Soc. London, **A109**, 351 (1925).

Table LXVII

Comparison of Maximal Conductivity Data, λ_∞, *in Methyl alcohol*, t = 25°

Compound	Hartley and Frazer observed	Walden computed
HCl	193.5	193.5
LiCl	90.9	90.9
$LiNO_3$	100.3	100.5
NaCl	97.0	97.0
NaBr	101.2	101.5
NaI	106.7	107.0
$NaNO_3$	106.5	106.6
KBr	109.4	109.4
KCl	105.05	104.9
KI	114.8	114.9
KNO_3	114.6	114.5

III. *In Ethyl Alcohol*, t = 25°

Given, Tetra-ethylammonium picrate: $\lambda_\infty{}^{25} = 51.5$ (Walden, Ulich and Laun)

Sodium picrate, $\lambda_\infty{}^{25} = 46.7$ (extrapolated from Goldschmidt's measurements)

The picrate ion in ethyl alcohol ($\eta^{25} = 0.01096$)

$$l_{Pi} = \frac{0.267}{0.01096} = 24.4$$

Therefore the tetra-ethylammonium cation

$l_{N(C_2H_5)_4^+} = 51.5 - 24.4 = 27.1$ (cf. above 27.02, Table LXI).

Further results are given in Table LXVIII.

Deserving of notice is the fact that Lenz's old transference measurements on potassium iodide are in good agreement with the ion mobilities calculated by Walden. Lenz found $n_K = 0.486$. From the limiting value $\lambda_\infty = 50.9$

TABLE LXVIII

		Ion mobilities:	
sodium ion	(from the picrate)	: 46.7 − 24.4 = 22.3	
iodide ion	(from NaI = 48.7)	: 48.7 − 22.3 = 26.4	
potassium ion	(from KI = 50.9)	: 50.9 − 26.4 = 24.5	
ammonium ion	(from NH_4-picrate)	: 46 − 24.4 = 21.6	
chloride ion	(from NaCl)	: 43.5 − 22.3 = 21.2	
lithium ion	(from LiCl)	: 39 − 21.2 = 17.8	
bromide ion	(from NaBr)	: 44.5 − 22.3 = 22.2	
NO_3^- ion	(from $LiNO_3$)	: 43.6 − 17.8 = 25.8	
Ag^+ ion	(from $AgNO_3$)	: 43 − 25.8 = 17.2	
$N(CH_3)_4^+$ ion	(from the chloride)	: 50.6 − 21.2 = 29.4	isomeric ions
$N(C_2H_5)_2H_2^+$	(from the chloride)	: 47.1 − 21.2 = 25.9	isomeric ions
$N(C_4H_9)H_3^+$ ion	(from the chloride)	: 42.3 − 21.2 = 21.1	isomeric ions
piperidinium ion	(from the chloride)	: 48.4 − 21.2 = 27.2	
piperidinium ion	(from the picrate)	: 51.7 − 24.4 = 27.3	
hydrogen ion	(from HCl)	: 83.6 − 21.2 = 62.4	
hydrogen ion	(from HI)	: 89.2 − 26.4 = 62.8	
hydrogen ion	(from HBr)	: 85 − 22.2 = 62.8	

and this transference number for the potassium ion, we obtain for the mobility

potassium $l_{K^+} = \lambda_\infty \times n_{K^+} = 50.9 \times 0.486 = 24.7$ (comp. above 24.5)

therefore

iodine $l_{I^-} = (50.9 - 24.7) = 26.2$ (comp. above 26.4).

H. A. Harned and Fleysher have determined the transference number of hydrochloric acid $n_H = 0.753$ at m = 0.001. If the transference number of the hydrogen ion in hydrochloric acid be calculated from previously given data, namely $\lambda_\infty = 83.6$ and $l_H = 62.8$, we obtain a value which is in good agreement with that found directly:

$$n_H = 62.8/83.6 = 0.751.$$

If the given transference numbers of some of the more widely investigated salts, such as lithium chloride,

sodium bromide and silver nitrate, be examined in the same way, one does not always find such close agreement. Thus

LiCl, calc. $n_{Cl} = 21.2/39 = 0.544$ (Drucker gives 0.58) (Lapworth gives 0.65)

NaBr, calc. $n_{Br} = 22.2/44.5 = 0.50$ (Drucker, gives 0.45)

$AgNO_3$, calc. $n_{Ag} = 17.2/43 = 0.400$ (Gibbons and Getmann found 0.379 by direct measurement, whereas Schlundt gives 0.405)

IV. *Acetone*, $t = 25°$

Given: Tetra-ethylammonium picrate $\lambda_\infty^{25} = 177.5$ (Walden, Ulich and Busch)

$$\text{Picrate ion } l_{Pi} = \frac{0.267}{0.003158} = 84.5$$

The resulting mobilities for various ions are given in Table LXIX.

TABLE LXIX

Cations:	From	Ion mobilities:
$N(C_2H_5)_4^+$	:(177.5 − 84.5)	= 93.0 (92.8 above)
$N(CH_3)_4^+$	the picrate ion:(187.0 − 84.5)	= 102.5
$N(C_3H_7)_4^+$	the picrate ion:(156.6 − 84.5)	= 72.1 (71.9 above)
$N(C_2H_5)_2H_2^+$	the picrate ion:(175.6 − 84.5)	= 91.1 } isomer
$N(C_4H_9)H_3^+$	the picrate ion:(176.6 − 84.5)	= 92.1 } $N(CH_3)_4^+$
Li^+	the picrate ion:(155.0 − 84.5)	= 70.5
Anions:		
I^-	$N(C_2H_5)_4I$:(209.0 − 93.0)	= 116.0 (116.2 Table LXIII)
Cl^-	$N(C_2H_5)_4Cl$:(198.1 − 93.0)	= 105.1
ClO_4^-	$N(C_2H_5)_4ClO_4$:(208.7 − 93.0)	= 115.7 }
ClO_4^-	$N(CH_3)_4ClO_4$:(218.5 − 102.5)	= 116.0 }
Also		
K^+	KI:(185.6 − 116.0)	= 69.6 (69.4 Table LXIII)
Na^+	NaI:(184.6 − 116.0)	= 68.6 (68.3 Table LXIII)
$\frac{1}{2}\,Ba^{++}$	$Ba(ClO_4)_2$:(201.2 − 115.7)	= 85.5

If we calculate the transference numbers of several of the more thoroughly investigated salts, *e.g.* sodium and

lithium iodides, from the above mentioned ion mobilities we obtain the following results:

$$\text{NaI, calc.}n_I = \frac{116.0}{184.6} = 0.628$$ (McBain and Coleman found 0.566 at v = 8.3)

$$\text{LiI, calc.}n_I = \frac{116.0}{186.5} = 0.622$$ (Sêrkov found 0.79 at v = 20)

$$\text{LiCl, calc.}n_{Cl} = \frac{105.1}{175.6} = 0.599$$ (Sêrkov found $n_{Cl} = 1.45$)

It would appear that the lithium halides, particularly lithium chloride, are rather abnormal in their behavior. Apparently they tend to form complex ions, possibly

$$(LiCl)_x \rightleftarrows Li^+ + (Li_{x-1}Cl_x)^-$$

It is also noteworthy that the mobilities of the alkali metallic ions bear a different relationship to one another in this solvent than in other media. Table LXX gives comparative data to illustrate this point.

TABLE LXX

Ion Mobilities of the Alkali Metals in Various Solvents at 25°

Solvent	K^+	Na^+	Li^+	K^+/Li^+	K^+/Na^+
Water	74.8	> 51.3	> 40.0	1.87	1.46
Methyl alcohol	53.9	> 46.1	> 39.9	1.35	1.17
Ethyl alcohol	24.5	> 22.3	> 17.8	1.38	1.10
Acetone	69.6	> 68.6	< 70.5	0.99	1.015

In water the ion mobilities of the three cations widely differ from one another. These differences are considerably smaller in ethyl alcohol, the relationship being approximately the same in both ethyl and methyl alcohol. In acetone the mobilities have become practically identical. If one assumes that this gradual equalization of these ion mobilities depends upon an adjustment of their ionic radii due to decreasing solvation of the Li^+ ions, it is justifiably conceivable that the solvation of the Li^+ and

Na^+ ions, respectively, may be decreased to such an extent in certain solvents that the order of mobilities may become completely reversed and

$$Li^+ > Na^+ > K^+$$

Examination of the measurements of Morgan and Lammert[1] in acetophenone with this idea in mind supports this assumption.

	LiCl		LiBr		NaI		KI	
λ_∞^{25}	40.0	>	39.6	>	38.22	>	37.22	(Morgan and Lammert)
λ'_∞	—		35?		40.4	>	39.8	(Extrapolated by Walden and Ulich)

A different order of mobilities apparently obtains here. It would be not without interest to repeat these measurements in acetophenone. Ethyl-methyl ketone might also be investigated to ascertain whether similar anomalies occur when this substance is used as solvent. Only two pertinent references in the form of equivalent conductivities at 25° are given in the literature:

KI, at v = 7692, λ_v = 102.7 (Philip and Courtman)

NaI at v = 7534, λ_v = 131.5 (Dutoit and Nicollier)

V. *Acetonitrile*, t = 25°

For purposes of orientation ion mobilities in acetonitrile, using the older measurements of P. Walden, are noted below.

Given: Tetra-ethylammonium iodide $N(C_2H_5)_4I$, λ_∞ = 194 (by extrapolation from the $\sqrt{c}$-formula)

Using $N(C_2H_5)_4^+$: l_K = 0.296 and the viscosity η = 0.00345, we obtain

$$l_{N(C_2H_5)_4} = \frac{0.296}{0.00345} = 85.8 \text{ (or 86 in round numbers)}$$

[1] J. Am. Chem. Soc., 46, 1117 (1924).

We may then calculate the following mobilities

Ion	From		l
Iodine	$N(C_2H_5)_4I - N(C_2H_5)_4^+$	$(194-86)$	= 108
Bromine	$N(C_2H_5)_4Br - N(C_2H_5)_4^+$	$(185-86)$	= 99
Sodium Na^+	$NaI - I^-$	$(190-108)$	= 82
Potassium K^+	$KI - I^-$	$(198-108)$	= 90

The mobilities of the sodium and potassium ions are here very nearly the same (see ethyl alcohol). For the transference number of the iodide ion, say in sodium iodide, we obtain, then, in the limiting case

$$\text{Iodide ion,} \quad n_{I^-} = 108/190 = 0.568$$

a value which is quite similar to that in methyl alcohol.

Mobility of Isomeric Ions.

The behavior of isomeric ions in aqueous solutions gave rise to the idea that they possess equal ionic velocities. It had already been pointed out[1] that this is wrong. Additional experimental evidence of tautomeric anions with different mobilities was presented by H. Ley.[2] Walden and his co-workers subsequently extended this work to isomeric cations and were able to prove that this difference was even more pronounced in organic solvents and in melts. The results of these investigations are noted in Table LXXI and deal with the cations $N(C_4H_9)H_3^+$, $N(C_2H_5)_2H_2^+$ and $N(CH_3)_4^+$, that is, with primary, secondary and quaternary ammonium bases.

TABLE LXXI

Ion Mobilities of Isomeric Cations

Solvents	*n*-$C_4H_9NH_3^+$	iso-$C_4H_9NH_3^+$	$(C_2H_5)_2NH_2^+$	$(CH_3)_4N^+$
Water (25°)	—	38.7	38.5	46.5*
Water (18°)	35.63	31.43	32.15	39.70
Methyl alcohol (25°)	—	47.8	57.3	65.5
Ethyl alcohol (25°)	—	21.1	25.9	29.4
Acetone (25°)	—	92.1	91.1	102.5
Picrates in the melt, t = 150° (molecular conductivity λ)	1.163	1.109	3.117	about 5

*Bredig, 1894.

[1] Walden, *Leitvermögen der Lösungen*, Pt. I, p. 347 and Pt. II p. 46 and 192 (1924).
[2] Z. physik. Chem., 106, 161 (1923).

This small tabulation is instructive in many respects. It shows in general that the tetra-alkylated ammonium cations have a larger mobility than the isomeric mono- and di-alkylated ions. These relationships exist not only in solutions of the salts, but also in the melt, free from any solvent influence. In the latter the difference between the mono- and di-substituted ammonium cations are specially pronounced. Ion mobilities—and the tendency toward dissociation—are dependent not only upon the nature and kind of atoms substituted in the cation, but also upon their steric arrangement.

SUMMARY

The mobilities of numerous ions in a whole series of solvents at 25° have been calculated beginning with the two large ions $N(C_2H_5)_4^+$ and $C_6H_2(NO_2)_3O^-$ (picrate ion) and using the $\lambda_\infty \cdot \eta$ = constant rule.

In so far as comparative data obtained by other methods exist, a satisfactory agreement was found to exist between the values calculated by Walden and those determined directly by other authors. Transference numbers were subsequently calculated from these ion mobilities and the corresponding maximal conductivities.

CONCLUSION

Let us return to the beginning of our discussions. "Strong electrolytes" were taken as the starting point for our considerations. A series of binary (uni-univalent) salts which were dissociated to practically the same degree, were chosen for experimentation. Previous investigation had given credence to the belief that these salts were all of one definite type. Was it not logical to assume that this similarity in behavior would remain unchanged in all solvents? It had long been recognized, indeed, that such acids as hydrochloric, trichloracetic, and picric, so-called "strong acids" in water, acted as very poor electrolytes in other solvents such as acetone, acetonitrile or nitro-

benzene (Walden). From the figures given in Table LXXII it is plainly evident that such a behavior is also characteristic of the typical ammonium salts.

TABLE LXXII

Conductivities of Typical Ammonium Salts in Various Solvents

Solvent	v	$N(C_2H_5)_4Cl$	$N(C_2H_5)_2H_2Cl$
Water	32	$\alpha = 0.861$	$\alpha = 0.866$
Ethyl alcohol	200	$\lambda = 31.3$	$\lambda = 30.0$
Acetone	1000	151.6	15.4
Methylene chloride	10	7.66	0.045
Chloroform	10	1.47	0.0018
Ethylene chloride	2000	23.0	(immeasurably small)

Use of various solvents eventually differentiates these two substances which we recognize as being of equal strength in aqueous solution. The first retains the characteristics of a strong salt, while the other gradually becomes weaker and weaker, finally to be classed as a non-electrolyte in ethylene chloride. The concept "strong salt," in so far as it has been deduced from conductimetric behavior in aqueous solutions, must be qualified by a statement of the chemical nature of solute and solvent. Just as the hydrogen salts, that is, acids, may grade from strong to weak electrolytes or to all intents and purposes become non-electrolytes, according to the nature of the solvent, so also may the alkylated ammonium salts, as well as the lithium and silver and other salts, vary in behavior depending upon the medium in which they are dissolved. Solvents may also effect a differentiation of the ions themselves. When combined with one and the same *cation* in aqueous solutions, the halide, nitrate and chlorate ions exert a dissociation effect which is practically the same. This effect is shifted to an appreciable degree in non-aqueous solvents, and salts formerly of equal dissociating power become of different strengths, assuming the following relative positions:

chloride < bromide < nitrate < iodide < perchlorate < picrate.

These findings make it possible to synthesize electrolytes or salts of varied "strength." It can be shown in this manner that salts of the best conducting type, that is those composed of a tetra-alkylated ammonium cation and of a picrate, perchlorate or iodide anion, give electrolytically conducting solutions even in the so-called "non-conductor" benzene.

On the basis of measurements presented, the rôle of the solvent in the conduction of a dissolved salt does not appear to be altogether simple. The selective solubility of salts, color changes and formation of solvates, seem to point to "chemical" relationships between solvent and solute. So far as physical properties of the solvents are concerned, it has been established that the dielectric constant, ϵ, and the viscosity, η, exert a very definite influence upon the "degree of dissociation" (i.e. $\alpha = \lambda_v/\lambda_\infty$) and the numerical size of the conductivity, respectively.

The $\lambda_\infty \cdot \eta$ = constant rule was verified for "strong" binary salts composed of large ions, after it had been demonstrated experimentally that the maximal conductivity, λ_∞, could be extrapolated with sufficient accuracy by the square-root formula. Extension of this rule subsequently led to a method for the determination of ion mobilities l_K and l_A and of transference number n in various solvents.

PART IV

STEREOCHEMISTRY AND OPTICAL (WALDEN) INVERSION.

CHAPTER XIII

Early History of Stereochemistry

"Wäre die Natur in ihren leblosen Anfangen nicht so gründlich stereometrisch, wie wollte sie zuletzt zum unberechenbaren und unermesslichen Leben gelangen?"—Goethe.[1]

Stereochemistry is an experimental branch of our modern chemical science. Stereochemical or stereometrical speculations and teachings, however, have been in some respects normal and characteristic expressions of chemistry since olden times. The human mind once proceeded to classify and define perceptible natural phenomena with but slight basis of theory and experiment. Everything that existed was matter. Man created his own time-space pictures of the external world. Size, form, position and movement were the chief mechanistic elements to whose variations all qualitative differences were traced.

The great classical thinkers, Leukipp and his youthful successor Democritus (about 460–360 B. C.) first suggested the atomic theory. Atoms are non-creatable, indestructible and non-changeable—all of the same non-qualified constitution. Nevertheless, they take up space, are impenetrable and are characterized by their infinitely variegated form, size and weight. Everything animate and inanimate is dependent upon the changing state and position, combination and separation, of atoms. Movement (also in the form of pressure and impact) brings forth such transformations.[2]

Plato (427–347 B. C.) gave definite geometrical forms to this original matter which had previously been with-

[1] "If nature in its inanimate origin were not so fundamentally stereometrical in character, how would it ever have attained the non-measurable and non-calculable Animate?"

[2] See E. O. von Lippmann, *Alchemie*, p. 133 (1919).

out qualities, that is, he removed it from the category of "non-existency" and assigned to it a condition of corporal reality; he gave boundaries and form to that which previously was assumed to be without form. He thus created individual substances. Consequently the four "qualities" or "elements" of Empedocles (500–430 B. C.), fire, water, air and earth, received regular stereometrical constructions. Fire was designated by tetrahedrons; air by octahedrons; water by icosahedrons and earth by hexahedrons. These were mutually and constructively interchangeable or underwent "reversible reactions." Thus,

$$1 \text{ octahedron air} \rightleftarrows 2 \text{ tetrahedrons fire},$$
$$1 \text{ icosahedron water} \rightleftarrows 2\tfrac{1}{2} \text{ octahedrons air},$$

and so the one form of matter might completely assume the nature of another; everything is interchangeable; one substance may easily be transformed into another.

Even Epicurus (341–270 B. C.) assumed all bodies to be modifications of a single, homogeneous, primary matter, whose particles possess a very definite form, are permanent and of an unchangeable nature. They must be arranged in a distinctly characteristic manner in order to yield the various materials which are found in this world. Some three centuries later a knowledge of these beliefs enabled the Roman poet Titus Lucretius Carus (96–55 B. C.) to incorporate these teachings of the Greek atomists, in detailed poetical style, in his work "De rerum natura."

Atoms with size, weight, form and movement were accepted as axiomatic, yet they were of no value so far as experimentation was concerned. The kind and sum of experimental data concerning the material world was still very limited; the interests of all those who would investigate and use such substances were directed toward other questions. Economic values were of primary importance. In consequence of the idea of a *materia prima*, investigators in succeeding centuries were captivated by a problem which had a practical aspect. Questions concerning the form of atoms, and the structure of matter were purely secondary. So a thousand years or more passed without

supplying a solution of this problem, but nevertheless yielding a more intimate and extended knowledge of the properties of the metals and their compounds.

FIFTEENTH CENTURY

Cusanus (1401–1464) was the first to suggest renewed consideration of the fundamental thoughts of atomism. Through processes of logic he arrived at an actual, indivisible mass, an atom, which represents a finite or limiting size. However, his thoughts found no resonance elsewhere.

SEVENTEENTH CENTURY

The seventeenth century is of particular importance in the development of our problem, first, because of the rejuvenation of atomism as such, secondly, because of the introduction of corporal atoms and corpuscles and their geometrical form into chemical theory. In his publication "De Chymicorum . . . ." which appeared in 1619, the German iatro-chemist, Sennert, comes out very emphatically in favor of the idea that all matter is composed of unchangeable, elementary particles or corpuscles, whose continued existence or the retention of whose identity and form throughout all chemical reactions is tacitly assumed.

The views of Descartes (Cartesius, 1596–1650), philosopher and mathematician, are striking in their mental perspective. Matter is characterized by dimensions; the ultimate components of matter are the corpuscles (corpuscula), that is, the smallest bodies which differ in form and size. Pressure and impact are sufficient to account for all natural phenomena. Matter and movement remain constant in quantity. His French countryman, contemporary, and philosophical opponent, Gassendi (1592–1655) was notably active in defending the old atomistic teachings. Matter is non-creatable and indestructible; it is divisible to an extreme limit, and these last particles are called atoms (or according to Cicero, *corpuscula*) which are to be distinguished by their size, form and weight. They may group together in different arrangements and posi-

tions to form "molecules".[1] The conception of molecules is undoubtedly used here for the first time.

Jungius (1587–1657), a contemporary of Descartes, is to be considered the chief exponent of atomism in Germany. Atoms are of given form and porosity, and because of "affinitas" and "ability to stick together" are able to combine to form "mixtures."

In his work "Ortus medicinae" (1648) van Helmont (1577–1644) made a novel application of these spatial conceptions. He regards water and steam as nothing else than water, and says, "No change in the nature of a substance occurs where only a spatial separation and withdrawal of the inner particles are concerned."[2]

However, a translation of such spatial ideas to chemistry, an incorporation of atomic structure as a mental aid in determining the significance of chemical reactions, had not yet taken place. Corporal atoms were only hypothetical building stones of matter; they were not to be thought of as components of individual substances or as the foundations and determinants of definite compounds. True enough, Jungius and Boyle (1661) did formulate the idea of chemical elements, but the practical evaluation of this postulation did not appear until several centuries later. The theory of chemical compounds also was still in process of evolution. New chemical facts were necessary before the problems of material composition, as conceived from the idea of elements, and of the structure of matter, could be solved.

Three chemists accomplished this preliminary chemical work in a historically memorable fashion. Not only did they increase the fund of chemical knowledge, but they

[1] Galileo Galilei (1564-1642), the physicist and astronomer, was evidently in favor of an extended application of the corpuscular theory. He says: "I do not believe that anything aside from size, form, mass, slow and rapid movement are necessary to excite in us taste, odor or sound." Do not his words sound prophetic when he says "The book of nature lies open before us, but it is written in letters different from our alphabet. Its letters are triangles, squares, circles and cubes."

[2] Even Comenius (1592-1670) in his *Physica*, Chapter VII, makes use of spatial conceptions to account for the various vapors and mists. He says "that bodies composed of the same qualities may assume this or that configuration or figure, frame work or form". (Strunz, *J. B. van Helmont*, note, p. 39 (1907)).

also incorporated the concept of corpuscles with definite form in their explanation of chemical reactions and the properties of chemical substances. Science certainly owes a debt to Glauber (1604–1670), Boyle (1627–1691) and Lemery (1645–1715). Glauber was particularly active from an experimental-preparative point of view, and helped to enrich chemical knowledge by his investigation dealing with salts and acids. Despite the fact that the corpuscular theory received little support from him, his work was of lasting value for the future theoretical development of the subject. He constantly practised the purification of substances by fractional distillation, and, in the case of salts, by fractional crystallization. He was probably one of the first to point out that crystal form is a characteristic of each salt type, and he recommended its use as a means of identification.[1]

That the corpuscular chemists should have provided these ultimate particles with points, hooks and pores, that is, that they should have ascribed to the corpuscles the forms of piercing, cutting and boring instruments, is probably due to the preference given to physiological reactions as a means of recognition of substances in general. The words "sour", "alkaline", "salty", are even today used as qualitative terms for chemical substances, being derived from the sensation of taste. Boyle defines a salt as follows: "It is easily dissoluble in water and it affects the palate with a savor whether good or evil." Since certain mechanical effects by means of sharp and pointed tools brought forth like sensations, it was only logical to assign similar structures to these corpuscles or atoms.

The French apothecary Lemery was the first to evolve a mechanistic corpuscular theory. He made use of this hypothesis in his textbook "Cours de Chimie", which first appeared in 1675. The wide publication of this work in French, Latin, German, English, Italian and Spanish, —a final edition appeared in 1756—gave it a profound directional influence throughout almost a century upon the theory of atoms and corpuscles.

[1] Glauber, *Opera Chymica* I, 1658, pp. 441, 526.

The geometrical forms of particles served as means of identification and as explanations for the like behavior of substances of the same class. Thus acids were believed to have one sort of construction and bases another. Even as today the common effective component of all acids is the hydrogen ion—a material substance with electrical charge, a proton—so did Lemery conceive of a geometrical design of particles which was identical in all compounds of this type. He says, "Acidity of a fluid is due to the presence of pointed particles. An acid is made up of pointed components." The strength of acids, the differing activity of the various acids are dependent upon the size and kind of "points" on the particles, or as Lemery expresses it "différence en subtilité de pointes."

Conversely, alkalies were characterized by rigid, brittle particles "dont les pores sont figurez de façon, que les pointes acides y estant entrées, elles brisent et écartent tout ce qui s'oppose à leur mouvement." In order that a given alkali may react with an acid it was necessary "qu'il y ait de la proportion entre les pointes acides et les pores de l'alkali." It appeared to be a question of steric agreement or steric hindrance. Chemical character and chemical relationship were thus determined by spatial factors, that is, by the form and the size of particles.

Salt formation through the action of acids upon metals, such as $AgNO_3$ from Ag and HNO_3, Bi and HNO_3, Pb and acetic acid, $HgCl_2$ and $Hg(NO_3)_2$, is, according to Lemery, an operation in which "the metal is penetrated and reduced to the form of a salt by the points of the acid." This salt formation always brings about an increase of weight in the case of metals, because the "points of the acid" are retained by the metal.

Even color was explained by stereochemical factors. With reference to the change in color which occurs when red mercuric oxide is treated with hydrochloric acid, Lemery[1] says: "On ne peut attribuer cet effet qu'au des arrangements que l'acide du sel fait des parties du precipité rouge et à la disposition où il les met, en sorte que leurs

[1] *Cours de Chymie*, p. 211 (1683).

surfaces soient en estat de faire refléchir la lumière en droite ligne à nos yeux pour nous faire paroistre une couleur blanche. Le precipité rouge ordinaire est donc capable des mêmes changemens que la dissolution du Mercure, sans que la couleur rouge luy donne rien de particulier; ce qui prouve encore fort bien que la couleur n'est rien de réel, et qu'elle ne dépend que de l'arrangement des parties." Only after two hundred years does the concept "*arrangement des parties*" attain a new meaning because of a new factual environment.

Boyle was notably active as a corpuscular chemist, both experimentally and theoretically. "Whatever may be the number of elements," he says, "one may someday probably be able to demonstrate that they exist as indefinable particles, nevertheless begotten of definite form and size, and that it is the *arrangement* and *combination* of these corpuscles which gives rise to the manifold number and varieties of bodies."[1] He theorizes concerning the origin of the form of matter and the relation between the latter and its properties, and he attempts to account for the particular crystalline habit of a substance by the form of its particles or corpuscles. The size of these corpuscules may be as small as desired. So far as their forms are concerned we have at our disposal a countless number of regular and irregular stereometric figures.[2] Chemical metathesis takes place when the corpuscles of one substance fit more or less definitely into the pores of another. A certain "congruity" is assumed to exist between both types of corpuscles.[3] Acids may dissolve metals when the pointed particles of the first are congruous with those of the latter. He compares acid particles to knife blades; some of these have only one end encased in a shield; in the case of others both ends have been put into a shield. Such an explanation is used to account for the existence of the two chlorides of mercury.

[1] *Sceptical Chymist*, 1661.
[2] Boyle, *Origin of Forms and Qualities*, 1664.
[3] Boyle, *A Natural History of Human Blood*, 1684.

The opinion of that famous mathematician and physicist, Blaise Pascal, (1623–1662), is also noteworthy. "Il faut dire en gros: celà se fait par figure et mouvement, car celà est vrai . . ." Huygens (1629–1695) supposes substances to be composed of one and the same material "dans lesquels on ne considère aucune qualité, . . . mais seulement des différentes grandeurs, figures et mouvements." The nature of a substance is purely secondary; size, figure and movement are everything.

EIGHTEENTH CENTURY

Chemical Affinity and Crystal Form

One outstanding idea seemed to sway chemical research during the eighteenth century, and that was the question of chemical relationship or affinity; in particular, its causes, its magnitude and the manner of its determination. It is just these continued attempts to express "degrees of relationship" numerically, which led steadily to a knowledge of fundamental stoichiometric laws and of the nature of chemical compounds. These investigations concerning "causes" brought out many ideas, but produced no satisfactory solution.

In an essay submitted for the prize of the Academy of Rouen (1758), Lesage ascribed the cause of chemical attraction and relationship to form, and to the sizes of the spaces between particles. It is evident that such a mechanistic explanation is in line with the ideas which were current in the previous century. It was Buffon (1707–1788), who subsequently threw new light upon the question of relationship and its modifying factors. The whole problem depends on whether or not Newton's Law of Gravitation may be applied to chemical attraction. "Form, which may be regarded as having no influence upon the effect of heavenly bodies upon one another, because of the distances involved, may mean everything where this spatial difference is very small or negligible." Newton's Law seems to be inapplicable where *figure* is to be reckoned with in addition to distance. Buffon closes with the prophetic remark,

"The intellectuals of future centuries will open up a new field by considerations of this kind, and may possibly even be able to ascertain the form of the elements."

Bergman[1] also regarded the figure of atoms and molecules as a co-determinant factor in chemical relationships and one which modified the law of affinity. The varied forms of atoms and their changing position must influence the law of gravitation. In his "Lehre von der chemischen Verwandschaft" published in 1777, Wenzel takes both time of reaction and the form (figure) of the reactants into consideration. He assumed that the tendency of substances to combine is in direct relationship to the form of their components. Even Guyton de Morveau introduces the idea of the influence of form in his considerations on the modification of affinity. He attempts to make the "inner attractive forces" dependent "upon the relationship of the form of the parts of one body with those of the other."[2] He believes in the idea of the unity of matter and says: "It is the modification of a homogeneous substance which gives rise to all the different bodies and elements; the modifying factors are density, porosity and form." (1777).

It thus appears that all of these investigators of affinity were generally in agreement with the more attractive and less logical opinion that form, figure, and the size of atoms and molecules determine and influence chemical relationship. Chemical character was relegated to the background. If one inquires as to the cause for the omission of the specific nature of matter in these discussions, it will probably be found in the attempt to translate the gravitational laws of Newton, *à tout prix*, from the macrocosmic to the microcosmic. The law of the attraction of heavenly bodies eliminates the factor of chemical character, since only the masses m_1 and m_2, as such, and their distance apart, e, $(\frac{m_1, m_2}{e^2})$ are taken into account. Since it had been ascertained experimentally that chemical reactions take

[1] *Opuscul. phys. et. chem.* III, 1786, p. 292.

[2] All these old ideas recur in a certain measure in our modern discussions of "steric hindrances" with regard to the velocity of substitution reactions.

place only in the immediate neighborhood of molecules, the idea was developed that the form of the reacting molecules might be introduced as a vital factor. The speculations of the 17th century had already attempted to solve the question of the form of particles in a qualitative manner and by means of mechanistic, tool-like images. It now became more and more necessary not only to determine this influence quantitatively but to obtain definite, fundamental evidence concerning *form itself*.

A new scientific idea was introduced towards the middle of the 18th century in a field which is closely related to chemistry, namely *crystallography* and mineralogy. Crystals from the mineral kingdom, which had heretofore served either as commercial raw materials or as curios for the mineral collector and fancier, became objects of scientific study of their form and figure. Such questions as the geometrical form of crystals, laws governing the formation of the latter, the active forces involved, the process of crystallization in general, solution, saturation and super-saturation,—all were the result of the creation of the science of crystallography. Names worthy of mention in connection with the beginning of these studies are those of the two great pioneers Romé de l'Isle and his French countryman René J. Haüy (1743–1822). The first of these defines crystallization[1] "as the property of assuming a form which is definite and determined for each variety." According to Haüy every chemical compound of a definite composition has a form peculiar to itself. Chemical composition and crystal form are therefore brought into intimate relationship with each other. The formation of crystals takes place in a manner similar to the construction of a building from building blocks, that is, by laying, one upon another, particles of a very definite form so that no space is left in between. By considering the geometrical properties of crystals as functions of the smallest crystal particles, and the arrangement of the latter in space, chemists once more became interested in the problem of the nature and form of chemical particles

[1] *Cristallographie*, 2nd Ed., I, 1 (1783).

and "corpuscles," and advanced new models to depict them. However, reaction against the tendency of overemphasizing form and pictoral illustration of crystals as means of qualitative classification of individual minerals soon set in. Cronstedt[1] decried those "who are so imbued with a *figuro-manie* and a taste for the external that they take offense when marble is said to be limestone and porphyry is counted among the igneous rocks."

NINETEENTH CENTURY

Geometrical Arrangement

The preliminary work of the eighteenth century almost immediately yielded an unusually rich harvest at the beginning of the nineteenth century. Retrospectively this period might indeed be called the beginning of modern chemistry. The discovery of Volta (1800) gave science in general, but chemistry in particular, an aid of incalculable potency. The old question of the cause of chemical relationship was steered into new channels. Electricity entered the world of chemical reactions; chemical forces in time became more and more definitely identified with electrical forces. (Davy, Berzelius, Grotthus, and others).

Dalton's "New System of Chemical Philosophy" (1808) was of prime importance in the further development of chemical thought and research. The atomic theory and its consequences, the law of definite and multiple proportions, atomic weights, atomic symbols, arrangement of atoms in chemical compounds, form of atoms and their points of contact—all were fundamental concepts of the newer and greater chemistry. They exerted a directional influence both on theoretical and experimental chemistry.

Discussing the further study and development of current opinions as to the mathematical proportions of the atoms, Wollaston stated in 1808—"We shall find the arithmetical relation alone will not be sufficient to explain their mutual action, and we shall be obliged to acquire

[1] *Versuch einer Mineralogie*, Vorrede (1770).

a geometrical conception of their *relative arrangement* in all three dimensions of solid extension."[1] However, he adds resignedly, "It is perhaps too much to hope that the *geometrical arrangement* of primary particles will ever be perfectly known." Wollaston discussed the various possible forms of arrangement of different kinds of atoms around a central atom. In the ratio 2:1, two atoms may attach themselves at the opposite poles of the atom which holds them all together; when in the ratio 3:1, they group themselves at the corners of a regular triangle, but when the number of one set of particles exceeds in the proportion four to one, then a stable equilibrium may again take place, if the four particles are situated at the angles of the four equilateral triangles composing a *regular tetrahedron*." Here indeed is the picture of the tetravalent carbon atom.

The conclusions drawn by Ampère (1814) are much more thorough and extended, and make it appear that he, along with Avogadro, was a co-creator of the molecular theory. He holds that the spatial arrangement of molecules rests upon the assumption of regular tetrahedrons and octahedrons, which are combined variously for different compounds. Twenty-three polyhedrons or "representative figures" are given. From the various forms Ampère[2] makes deductions concerning degrees of combination, solubility, degree of hydration (water of crystallization), quantity of acid or base in acidic or basic salts. In later years Ampère again referred to the distinction which he had made between *particles*, *molecules and atoms*. "Molecules are groups of atoms which are kept apart from one another by the attractive and repulsive forces of each individual atom. From this definition of molecules and atoms it follows that the molecule is a rigid body, that the substances to which it belongs may be solid, liquid, or gaseous, that the molecule has a polyhedric form[3] in which its atoms, or at least some of them, occupy corner positions."

[1] Trans. Roy. Soc., London, **98**, 96 (1808).
[2] Ann. chim. **90**, 43 (1814); see also Ostwald's *Klassiker* No. 8, 23.
[3] Ann. chim. et phys., **58**, 432 (1835).

Another famous physicist, Biot, who dealt with the molecular composition of light, should be mentioned here. He advanced the theory of the material composition of light, and assumed that light is made up of fine matter consisting of molecules. He speaks of "molécules de lumière," even gives them stereochemical form, and seeks by means of them to explain the polarization of light.[1]

Thus we see that geometrical figure and spatial arrangement are the logical results of the extension of the fundamentals of crystallography, as well as of the atomic (Wollaston) and molecular (Ampère) theories. Even so critical and cautious a scientist as Berzelius commented frankly on the matter. "It is a bit far fetched to think of the atoms or molecules of compound bodies as existing in the form of spheres. It is much more logical to think of them as possessing regular figures which are dependent upon the number and kind of simple atoms combined to form the compounds."[2] "In the meantime a continued study of crystal atomism, basic forms and integrant molecules should in the future cast more light on the subject."

Opinions had already crystallized to such an extent a hundred years ago that Chevreul set up the following characteristics for a "chemical type": "In the case of compound bodies, a species is a collection of individual particles, identical in their nature, their proportions and the arrangement of their elements."

New facts served to make the problem of atomic structure more and more the focal point of the newer chemistry. One of these was the discovery of isomorphism by E. Mitscherlich (1819), according to which substances of different chemical composition, such as KH_2PO_4 and KH_2AsO_4, but of the same number of atoms, may have the same crystal form. "Crystal form is independent of the chemical nature of atoms and is determined only by the number and relative position of the atoms."[3]

[1] *Précis élémentaire de physique expérimentale*, Paris 1818-1821.

[2] Berzelius, *Versuch über die Theorie der chemischen Proportionen* (1819). German Edition by K. A. Bläde, 1820 p. 25.

[3] Ann., **19**, 419 (1821).

The fact that substances exist which have the same composition but are nevertheless different physically and chemically—practically the opposite of Mitscherlich's observations—was recognized soon afterwards. Facts of this kind form the so-called isomeric phenomena. Gay-Lussac[1] concluded "that the same components are able to combine in many different ways." Berzelius expressed himself similarly in that he postulated the existence of substances "which are composed of the same number of atoms of the same elements, but are arranged in different ways." Dumas assumed "un certain arrangement moléculaire"[2] or "a dissimilar relative position" of the atoms. His attempt to bring chemical elements into an isomeric relationship with one another is also interesting. Platinum he thought to be isomeric with iridium; cobalt with nickel; and molybdenum was assumed to be isomeric with two atoms of tungsten.

Berzelius next defined his concept of "isomerism" more accurately by distinguishing the latter from polymerism and metamerism. On the basis of his idea of isomeric substances—those having the same relative and absolute number of atoms of the same elements—Berzelius seemed to find ground for the assertion that atoms "may arrange themselves in various positions with respect to one another." However his postulations deal more with the idea of a saturation change.[3]

Gaudin[4] and Baudrimont[5] published their opinions as to form of the atoms about the same time. Gaudin writes, "Il serait plus facile de fixer le nombre des atomes contenues dans ces groupes appelés molécules . . . et par suite, en étudiant les crystaux, de pressentir la disposition relative et celle de molécules entre elles . . . en effect, s'il nous était donné de connaître au juste la forme d'une seule molécule, qui doute que nous ne puissions bientôt

[1] Ann. chim. phys., **27**, 199 (1824).
[2] Ann. chim. phys., **47**, 324 (1831).
[3] Jahresber., 1833, p. 64.
[4] Ann. chim. phys., **50**, 198; **52**, 113 (1833).
[5] J. chim. méd., **9**, 40 (1833).

découvrir le reste?" Berzelius[1] expressed the following opinion regarding such theoretical ramifications: "This whole theory may be only a play of the imagination, but the idea of the existence of groups of atoms even in the gases of simple substances is admittedly very fascinating. Definite crystal forms of simple bodies and the tendency to take such forms can be explained only by assuming the existence of an inherent tendency to group in a certain particular way." He again makes mention of this problem a year later: "It is certain that we cannot determine how atoms are arranged with respect to one another; however, it is just as certain that every substance is characterized by a definite order or arrangement, without which it would not have the properties which it possesses."

Liebig expressed a similar opinion in his "Handbuch der Chemie."[2] The significance of crystal form in determining the constitution of chemical compounds is emphasized by his statement: "In this work we regard the connection of external form with chemical composition as the most definite guide for instructing us as to the chemical constitution of compounds." No less definitely and convincingly does Liebig write with reference to the causes of isomorphism and the like chemical behavior of isomorphous bodies: "The most logical course is to look for these (causes) in the like form and arrangement of the smallest particles which they assume in their compounds. It follows therefrom that atoms are really existent, and all this may be regarded as evidence that the atomic theory is something more than a product of the imagination."

These statements seem to indicate that as early as 1840 the reality of atoms and of atomic structure, and the tendency of atoms to take up spatial-crystallographic arrangements as evidenced by the facts at hand, were commonly accepted mental premises both in organic and inorganic chemistry.

Rapid strides were made at that time particularly in organic chemistry. To the list of isomeric substances a pair

[1] Jahresber., 1834, p. 14; 1835, p. 86.
[2] Pt. I, p. 761 (1837-1843).

of acids had been added which were soon to play an important part in the further development of steric concepts, namely, racemic acid (Gay-Lussac 1826), isomeric with tartaric acid. The replacement of electropositive hydrogen by electronegative chlorine (Dumas 1834) also led to new experiments and theories, and Dumas proposed his theory of substitution.

In 1835 Laurent began his investigation of the chlorination products of naphthaline, and in 1837 developed his "kernel" theory. Haüy's theory of crystal structure really served as the model, and Laurent applied it to organic molecules. Both have a "kernel." Just as a crystal may be split mechanically to separate the primary kernel from the secondary shell or the material which encloses the first, so the kernel from the molecular-chemical point of view may be regarded as a geometrical body composed of atoms—say, a sixteen-sided column—in which the individual atoms are exchangeable, and to which other molecules may attach themselves as "secondary shells" to give outline to the structure.

Spatial models of organic molecules began to play an increasingly important part in the ideas of chemists. Whereas Laurent pictured rigid crystals with kernel and outer shells, Dumas thought of them as similar to our planetary system in which atoms, held together by their respective affinities, take the part of the individual planets.[1] Thus we find the following definition by Gerhardt: "We consider all substances, be they simple or compound, as similar to an edifice or to a unique system which is made up of a collection of infinitely small and indivisible particles called atoms arranged in a definite but unknown order. This system is called the molecule of a substance."[2]

Leopold Gmelin deserves much credit for the ingenious way in which he aided in the development, and discussed the consequences, of these steric views, especially Laurent's "kernel theory." In his "Handbuch der organischen

[1] See Wurtz, *Geschichte der chemischen Theorien*, p. 73 (Berlin, 1870).
[2] *Introduction a l'étude de la chimie*, p. 55 (Paris, 1848).

Chemie"[1] he presents for the first time an outline of the stereochemistry of inorganic and organic compounds. He says: "Chemists in general accept the atomic theory; they determine the relative weights of atoms; the relative distances of one from the other or the relative amount of space which each atom of a compound occupies, together with its surrounding energy layer. One makes assumptions regarding the form of atoms, etc., why should we not also theorize about the relative positions of the atoms in compounds?" The form given to the individual atoms should be compared with the crystal form of the salts themselves. Cubes, pyramids, etc., are assumed to be the most common crystallographic habits of compounds or organic "kernels." Thus Gmelin arrived at theories which did not again take on a new lease on life until fifty years later. He discusses acetic acid, saying that "only one of hydrogen atoms outside of the kernel is replaceable by metals." Do we not today hold the same idea when we write the formula for acetic acid as $(CH_3COO)H$, or when we assume the varied ease of replacement of hydrogen atoms to be due to their "varied position?" Does it not seem quite modern when Gmelin speaks of the influence of other atoms, even though these be far away, upon the process of substitution? He states that the hydrogen atom is "protected against the withdrawing influence of chlorine by certain groups or atoms, or by their spatial transmigration." During the course of certain reactions "a rotation of the kernel," a change in the "axis of the cube," may take place. Today we speak of "steric hindrance," and of the "rotation," "transition" or "migration" of atoms in a molecule.

After 1848 Gmelin no longer took part in the development of his own theories, despite the fact that he correctly predicted the direction which the science would take: "Whether the position of the atom, as it is here supposedly outlined, is the right one or not, atomists will, nevertheless, have to admit that atoms are not arranged in a row next to each other as one would be led to believe from the

[1] 4th Edition, Heidelberg (1848); pt. I, p. 27-33.

usual symbolization, but that they assume, by virtue of their affinities, more or less regular, corporal figures. It is of greatest importance to ascertain this position with some degree of probability, not only since light may thereby be cast upon crystal form, isomerism, and allied phenomena, but also because we may, through such considerations, arrive at a proper conception of the constitution of organic compounds."

Mention may here be made of another theory which was advanced at about the same time and discarded as too phantastic. In 1845 Millon[1] published some original ideas on the difference between organic and inorganic compounds, discarding the idea of radicals.[2] Berzelius criticized these views as extremely faulty. According to Millon, the difference between the two classes of compounds rests in the fact that inorganic substances owe their properties to the "juxtaposition of the atoms" (i.e. a position of atoms side by side). In the case of organic compounds, the atoms may *penetrate one another*, since the atoms of carbon, which are always present in bodies of this latter class, are permeable. "Carbon atoms, which in all organic nature are permeated with hydrogen, nitrogen and oxygen, form a new class of substances that act not through the medium of their components, but in their entirety. . . . True enough, the organic molecule opens itself for substitution reactions, but it conserves its stability because of the number of its elements."

The idea of the "juxtaposition of atoms" in inorganic compounds (electrolytes) reminds us of salt (ionic) lattices. The suggestion of the penetration of carbon atoms in organic compounds is similar to the conception of electronic penetration of shared electrons in homeopolar molecules.

One of the world's most famous philosophers also takes up the idea of the corporal reality of the atom. After he had investigated the evidence which had been

[1] Ann. chim. phys., (3) **13**, 385 (1845).
[2] Jahresber., **26**, 400 (1847).

presented to prove the existence of the atom, Schopenhauer[1] said that if one takes for granted the atomistic structure of matter . . . "then atoms, that is, absolutely indivisible particles, do exist. . . . However, one can assume these to be not only small, but also very large. An atom might be as large as an ox, provided it resisted every possible action!"

Racemic Acid. Pasteur's Researches (1848-1860).

A mighty impulse was provided by crystallography, particularly by the crystallographic study of organic compounds. The names de La Provostaye (1841), E. Mitscherlich (1844), and Louis Pasteur (1848) are particularly prominent. The first-named carefully determined the crystal forms of tartaric and paratartaric acids and their salts. Soon thereafter Mitscherlich published the results of his crystallographic investigations of the sodium-ammonium salts of racemic and tartaric acid, stating that these double salts "have the same chemical composition, same crystal form and angles, identical specific weights and double refractions, in consequence of which their axes form the same angles. Their aqueous solutions have the same refraction. However, the dissolved tartrate rotates the plane of polarized light, whereas the other is indifferent, a fact which had previously been noted for this whole series of salts, by Biot. The nature and number of atoms, their arrangement and their respective distances from one another, are the same in both of these substances."[2]

As is often the case in the growth of ideas which do not come to full fruition until a later time when repetition of experimental work is necessary, we find the history of stereochemical theories repeating itself twenty-five years later with amazing results. The investigations of Mitscherlich in 1844 made a deep impression upon the mind of a gifted youth, Louis Pasteur, twenty-two years old (1822–1895). Unknowingly, this impression was a lasting one and several years later (1848) acted as a directional stim-

[1] *Welt als Wille und Vorstellung*, Second Edition, Book II, Chapt. 23.
[2] See Biot's report, Compt. rend., 19, 719(1844); also Ostwald's *Klassiker* No. 28, p. 12.

ulus for a whole series of new experimental and theoretical investigations when the opportunity presented itself. The same sort of thing happened in 1874 when the young J. H. van't Hoff (1852–1911) conceived the idea of the asymmetric carbon atom while studying a paper by Wislicenus.

But to return to Pasteur. It is extremely instructive to learn how logical the course of the development of ideas may be, even though the participants are not cognizant thereof. Hauy and Weiss had long ago discovered that hemihedral surfaces occur on quartz, and that in some specimens these face left, in others, right. Biot (1813) found that quartz crystals could be divided into two groups with reference to their behavior towards polarized light. One variety rotates the plane of polarized light to the left, the other to the right. Two years later he discovered that organic liquids (oil of turpentine), aqueous solutions, (sugar, tartaric acid) rotate the plane of polarized light. Therefore the property of optical rotation is not limited to crystals, such as quartz, but also occurs in amorphous and dissolved substances. It was also shown to occur in the vapor state,[1] as in the case of the vapor of turpentine. Herschel subsequently observed (1820) a connection between crystal form and optical rotation or the direction of the rotation. Quartz crystals with left hemihedral faces turn the plane of polarized light to the left, and those with right faces turn the plane to the right. Since these phenomena are characteristic of crystalline, as well as of dissolved and vaporized substances, provided that they are of definite chemical composition, Herschel concludes: "Whenever such a phenomenon becomes apparent, we must regard an *individual molecule as built up asymmetrically*."

The hypothetical crystal kernels and visible hemihedral faces had led by way of amorphous substances to the idea of asymmetrically constructed individual molecules. A new physical experimental aid, polarized light, assisted in this change of views. All this happened at the time when the 25-year-old philologist Mitscherlich—one

[1] Biot (1817).

could almost say, before he had become a chemist—completed in 1819 his epoch-making chemical discovery of isomorphism by crystallographic investigation. It is quite a coincidence that several decades later the young Pasteur became a discoverer through his crystallographic studies, at the beginning of his own chemical researches. The number and kind of physico-chemical methods was then quite limited, and among them crystallography occupied a very important position. To obtain practice in this method, Pasteur chose to repeat the previously mentioned investigation of de La Provostaye. In so doing he noted something which had never been reported before, namely, that all crystals of the tartrate possessed hemihedral faces. Since solutions of the tartrate also rotate the plane of polarized light to the right (comp. Biot), the same sort of parallelism exists between hemihedrism and optical rotation for tartaric acid and tartrates, both in the crystalline state and in solution, as had previously been found by Herschel to be true of quartz. Indeed, in the case of racemic acid and its salts, Pasteur found no hemihedral faces, and, curiously enough, Biot had previously shown that aqueous solutions of this acid and its salts remained inactive towards polarized light. Thus far, everything agreed beautifully. But how were these facts to be harmonized with the observations of Mitscherlich, who had found, in 1844, that the crystal forms of sodium-ammonium salts of racemic and tartaric acids are completely identical?

Here again the element of "chance" in chemical discoveries must be emphasized. A very important part is played by the purely accidental fact that "double salts" were chosen by Mitscherlich for his investigations. Pasteur now repeated this work with the utmost care, and observed to his surprise that the double salt of racemic or paratartaric acid would crystallize with hemihedral faces, some of which were oriented to the right, others to the left. By separating the two types of crystals from one another, and then examining the aqueous solutions of each with reference to their rotatory power, he found that solutions with *right* hemihedral faces were dextro-rota-

tory, and that an equally concentrated solution of crystals of the opposite, *left* hemihedral, character rotated the plane of polarized light to the left to an equal extent. Further, on mixing the two solutions, optical activity disappeared. The two types of crystals were isomorphous. However, "It is the *isomorphism of two asymmetrical crystals having the relation of object and image to each other.*"[1]

Thus did Pasteur discover the first of his classical methods for the separation of racemic substances into their optical antipodes. The second, salt formation by means of optically active bases and subsequent fractional crystallization, followed in 1853. The third method, involving the destruction of one of the active forms by means of microorganisms, was announced in 1858.[2] In 1860 Pasteur summarized his researches in his two famous lectures "Concerning the asymmetry of naturally occurring organic compounds."[3] These served as the basis for his own researches and as the foundation for the further development of stereochemistry. At the same time his inspired remarks served to advance the idea of the influence of molecular asymmetry of natural organic products upon living organisms, and promoted discussion and experimentation. It is, as he says, a chapter "which opens up new, distant, but distinct horizons for physiology."

Pasteur divides molecules into two classes with respect to their form:

(1) Those whose mirror images are superimposable with their own (straight steps, cubes, etc., may serve as models which possess a symmetrical structure).

(2) Those whose mirror images do not coincide, but which exist in oppositely constructed enantiomorphic forms (spiral staircases, right- and left-handed threads, the right hand and the left hand, irregular tetrahedrons).

With reference to the structure of the optically active tartaric acid, Pasteur asks: "Are the atoms of the dextro-

[1] Pasteur, Compt. rend., **26**, 535; Ann. chim. phys., (3), **24**, 442 (1848); **28**, 56 (1850); **38**, 437 (1853).
[2] Compt. rend., **46**, 615 (1858); **51**, 298 (1860).
[3] See Ostwald's *Klassiker*, No. 28, 1891.

acid grouped in the form of a dextro-spiral, or do they occupy positions at the corners of *irregular tetrahedrons*, or do they assume one of several asymmetric arrangements? That we do not know. However, there is absolutely no doubt that we are here dealing with an asymmetric order whose pictures are not congruous."

These classical researches and discoveries of Pasteur are important not only because of the new facts and conceptions which they directly introduced, but also because of their influence on the theories and experimental work of the following epoch. The chronologist of discoveries can learn from this series of investigations how tenacious, logical and exact the work of a discoverer must be. Laplace was right when he said: "The essence of a discovery lies in the combination of ideas that are fit for combination and that were hitherto isolated."

A survey of the advances up to this point make it plainly evident that the chief credit for the solution of the question of molecular structure was due to crystallographic investigations. Such studies, in connection with the use of polarized light, brought the old chemists appreciably nearer to a true understanding of molecular constitution.

The next step in the development was primarily dominated by chemical research. It finds its present conclusion in crystallographic research by means of X-ray photography.

The Structure of Molecules.

The theory of chemical valence opened up the discussion of the structure of molecules from an entirely new point of view. On the basis of Avogadro's hypothesis (1811), determination of molecular weight had been made possible by the vapor density methods of Gay-Lussac, Dumas (1827), and Gay-Lussac–Hofmann (1868).

Thanks to the efforts of Gerhardt (1850) and Canizzaro (1858) the use of molecular weights in inorganic, and particularly in organic chemistry, had found more general acceptance, aiding materially in the clarification of chem-

ical formulas. Frankland's theory of valence (1851) shed new light upon the interchangeable order of atoms in the molecule. Because of the tetravalency of carbon, a fact which had been suggested very specifically by Kekulé (1858), it became both possible and necessary to depict structurally the large and varied class of organic compounds. A *graphical* representation of atomic linkage was required, and so for the first time two-dimensional formulas appeared. Not long after, three-dimensional pictures of corporal molecules and atoms were thought necessary.

In this connection Butlerow deserves prominent mention; he has been called the creator of the concept "chemical structure." He expressed himself as follows in 1862: "Let us take a simple example, and, assuming that all four valency units of tetravalent carbon are different, let us give it the form of a tetrahedron where each of the four surfaces may combine with one equivalent of hydrogen."[1] In 1863 he came forward very decisively in favor of the idea of spatial arrangement, "If atoms really exist, I cannot see why all attempts at determining their spatial arrangement are useless, as Kolbe would have us believe. Why should not the future teach us how to make such determinations?" His words are prophetic when he says, "The chemical behavior of each individual atom in a compound molecule, be it any element whatsoever, is regulated on the one hand by its nature and chemical position in the molecule, and, on the other hand, by the nature, number and chemical position of the other atoms in the molecule."[2] He says, furthermore, in words which anticipate our modern atomic and molecular physics, "It is to be hoped that the laws which control formation and existence of chemical compounds may some day be expressed mathematically."[3]

These statements of Butlerow clearly indicate that he was far ahead of his time, and that he was a steadfast defender of the idea of spatial arrangement. He expressed

[1] Z. Chem., **5**, 297 (1862); *see also* Gelehrte Schriften der Universität Kasan, 1862.
[2] *Lehrbuch der Chemie*, Kasan, Russian Edition (1864); German Edition (1868) p. 720.
[3] Z. Chem., **5**, 504 (1863).

the hope that chemical research would result in the mathematical formulation of relationships between the atoms in a molecule. As science progresses, it often happens that a person in his later years lives to see his ideas and youthful dreams materialize without taking any active part in their further development. When, shortly, afterwards, van't Hoff created stereochemistry, Butlerow manifested no further interest in this subject.

As early as 1864 Heintz deemed it necessary that "chemical formulas give an approximate picture of the position of atoms in a corporal molecule." This requirement was met by Kekulé who said: "The incompleteness of the older models may be avoided if the four valencies of carbon, instead of being represented on a plane, are directed along the axes of a hexahedron starting from the atomic sphere itself and ending in the planes of a tetrahedron."[1] An attempt was made to explain the constitution of mesitylene in accordance with this principle. Two years later Paternò (1869) attempted to give spatial chemical forms to the isomers of $C_2H_4X_2$; "it is only necessary to arrange the four valencies of carbon as the four angles of a regular tetrahedron." Ladenburg[2] also advanced his prismatic formula for benzene in that year. Rosenstiehl proposed the representation of C_6H_6 by six tetrahedrons. In the same year (1869) Wislicenus definitely determined that there are three modifications of hydroxypropionic acid. "Facts such as these will make it necessary to explain the existence of different isomeric molecules of the same structural formula by the varied position of atoms in space. New conceptions are in order."[3] In explanation it might be mentioned that Wislicenus had investigated sarco- or d-lactic acid as well as β-hydroxypropionic acid and ordinary lactic or α-hydroxypropionic acid. Some decades before this, an optically active tartaric acid and the inactive racemic form had led Pasteur to formulate chemical-spatial concepts.

[1] Z. Chem., N. F., **3**, 218 (1867).
[2] Ber., **2**, 140, 272 (1869).
[3] Ber., **2**, 550, 620 (1869); Ann., **167**, 343 (1873).

These numerous investigations are characteristic of the tendency[1] of chemists of that time to give corporal form to atoms and molecules. It is quite logical from the standpoint of mental *actio et contractio*, that a discussion took place in the same year (1869) at the instigation of the London Chemical Society, concerning the justification of the atomic theory in general. Williamson had to defend the atomic theory against the earnest and serious attacks of leading English chemists![2]

In 1873 Wislicenus[3] published a long article upon the lactic acids. He explained the many cases of isomerism "by the varied spatial position of the atoms which are combined with one another" and proposed the term "*geometrical isomerism*" for this particular type of isomerism. Thus he coined the classical designations "spatial position" or "position in space" and "geometrical isomerism" for the portentous discoveries which were to become of such infinite value in the development of the whole problem. This brings the question to the point where van't Hoff and LeBel began their great work.

van't Hoff and LeBel as Founders of Modern Stereochemical Science (1874)

In September 1874 there appeared in Utrecht a small Dutch pamphlet whose author, J. H. van't Hoff, revealed himself at the end of the article. Its lengthy title was: "Proposal for the extension into space of current chemical structural formulas with attendant remarks concerning the relationship between optical rotatory power and the chemical constitution of organic compounds."

[1] Even as late as 1868 Mohr (*Mechanische Theorie der chemischen Affinität*, Braunschweig, 1868, p. 286) criticized the idea of position of atoms as follows: "A much too vulgar mechanical concept has been introduced by the idea of position of atoms. . . . We must do away with this thought altogether, lest we fall into the unclean. . . . Our whole chemistry deals only with the quantities of ponderable matter, and a meagre description of melting point, boiling point, specific weight or specific heat is thrown in with the bargain." It seems hardly conceivable to us today, that such unpretentious tasks and experimental aids as those which the chemistry depicted by Mohr would employ, should refer to the chemistry of only 60 years ago!

[2] Ber., **2**, 616 (1869).

[3] Ann., **167**, 343 (1873).

A more detailed edition of this essay appeared in 1875 in the French language under the title: "La chimie dans l'espace." In 1877 a German edition appeared with a preface by Wislicenus, who not only acted as defender and champion of van't Hoff's views, but also coined a name for this new science and gave it powerful support. In 1904 van't Hoff wrote: "At that time (1873) I had been studying Wislicenus' publication on the lactic acids, at the University of Utrecht, and when about halfway through the article, I decided to stop my work and take a walk. It was during this walk, under the influence of fresh air, that the idea of an asymmetric carbon atom occurred to me."

At about the same time (November 1874) LeBel[1] published independently an article expressing similar views on molecular asymmetry and optical rotation, in which he went back to the investigations of Pasteur.

The writings of these two investigators demonstrate once again, how the facts and ideas of past times may become the germs of the investigations of the future; how modern knowledge is fundamentally linked with earlier facts; and how continuous and logical is the process of development of science.[2]

The Main Points in the Teachings of van't Hoff.

Let us consider the saturated tetravalent carbon atom. For purposes of simplicity we will exclude from the discussion the movements of atoms, and will

I. Consider the molecule as a stable system of material points, and

II. Assume that the four valencies of the carbon atom, which are equal with one another, are directed to the corners of a regular tetrahedron.

The result will depict a spatial picture of an asymmetric carbon atom; in the center of the tetrahedron is the C-atom itself, and the four corners are occupied by four

[1] Bull. soc. chim., 1874, ii, **22**, 377.

[2] Detailed facts concerning the development of stereochemistry are given in the lectures by Walden entitled "Fifty Years of Stereochemical Research." Ber., **58**, 237 (1925); Naturwiss. XIII, N. N. 15-18 (1925).

different atoms or atomic complexes in firm positions. Such an asymmetric carbon atom may exist in two isomeric forms, as object and image.

Every dissolved substance possessing rotatory power must contain at least one such asymmetric carbon atom.

These assumptions of van't Hoff lead directly to the following conclusions:

First:—Substitution at one of these four corners should not change the whole system or the mutually firm positions of the other three radicals or atoms.

Second:—The change of the rotation, or, more exactly, the inversion of the sign and magnitude can be caused only by the inversion of the whole asymmetric atom, i.e. the interchange of object for image, and *vice versa*.

As a special chapter of stereochemistry, one which in particular deals experimentally with both of the last mentioned deductions, and one which has led to unexpected results, we may place the so-called optical inversion phenomena (Walden Inversion, 1895 and following years). These are briefly recorded in the following pages.

In a monograph[1] Walden attempted to collect all the literature available on this subject up to 1918. Research since then has produced much additional experimental and theoretical material. The most prominent workers in this field include since 1918: McKenzie and his co-workers, Senter and co-workers, Karrer and Kaase, Clough, Lowry, W. A. Noyes, Kenyon, Phillips, Levene and Mikeska, Holmberg,[2] Kuhn and Ebel, Meisenheimer, Hückel,[3] and others.

[1] Walden, *Optische Umkehrerscheinungen*, Fr. Vieweg, Braunschweig, 1919.

[2] This investigator recently published a very comprehensive lecture concerning the "Walden Inversion", Svensk Kem. Tid., 39, 1–19 (1927).

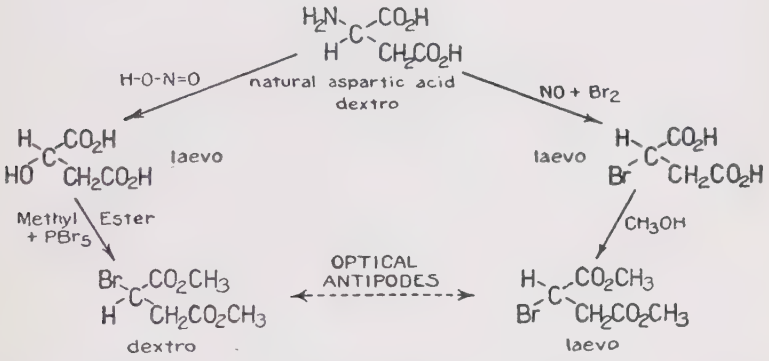
[3] Z. angewandte Chem., 39, 842 (1926).

CHAPTER XIV

B. Optical Inversion Phenomena (Walden Inversion)

THE STABILITY OF OPTICALLY ACTIVE SUBSTANCES

In 1895 Walden[1] made known the following remarkable stereochemical changes:



The next year he added reactions for the retransformation of the halogen acids into the hydroxyacids[2] and gave the "optical circle"—Fig. 13.

These are the experimental starting points of the so-called "Walden Inversion." The theoretical evaluation of this phenomenon may be illustrated by the opinions of several of the leading chemists of that time. In his judgment of the findings of Walden, W. Ostwald makes a statement which savors somewhat of hidden sarcasm. He says "the significance of these discoveries for the current spatial theories is an open question; one may indeed be highly expectant of efforts which will be made to explain this contradiction."[3]

[1] Ber., 28, 2769 (1895).
[2] Walden, Ber., 29, 133 (1896).
[3] Z. physik. Chem., 21, 189 (1896).

A decade later the study of this phenomenon entered into a new state. It was Emil Fischer who proposed the term "Walden Inversion,"[1] and who pointed out its significance. "This discovery is the most surprising observation in the field of optically active substances since the fundamental

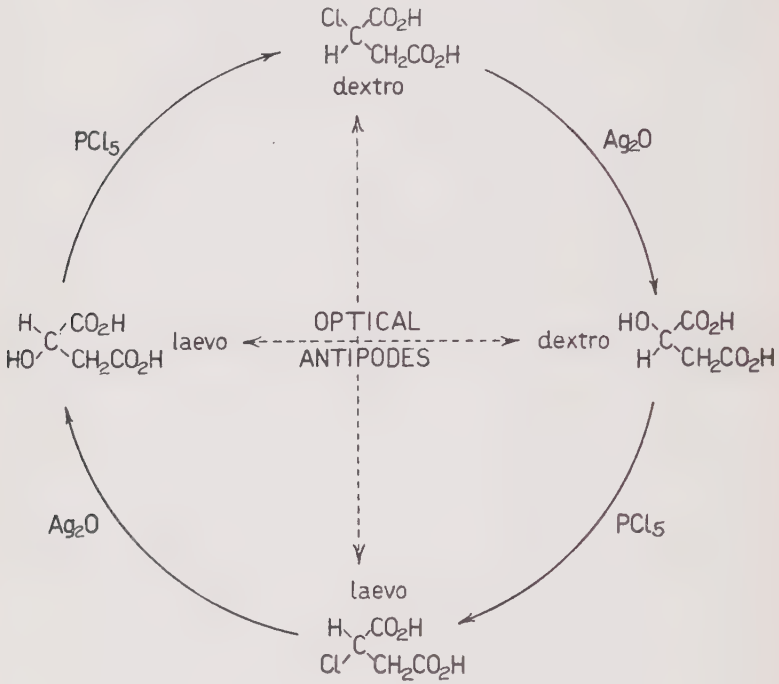


FIG. 13

investigations of Pasteur."[2] New experiments were carried out by him, and he later brought forward a theory to explain the inversion.[3]

New facts and further theories were soon advanced in explanation of this phenomenon. In 1913 Frankland[4] devoted a very comprehensive presidential address to the

[1] Ber., **39**, 2894 (1906).
[2] Fischer, Ber., **40**, 489 (1907).
[3] Fischer, Ann., **381**, 123 (1911); **386**, 374 (1912); **397**, 350 (1912).
[4] J. Chem. Soc., **103**, 713 (1913).

"Walden Inversion" in which he said: "Walden's discovery was certainly a puzzle and a surprise, for it did not fit into any pre-existing theory of optical activity, and had not been anticipated as a corollary to van't Hoff's theorem of the asymmetric carbon atom. It is highly probable that it may mark an epoch in our views with regard to the mechanism of the process of substitution in general."

What is today the consensus of opinion concerning this phenomenon, three decades after its inception? The following quotation gives answer to the question. "In the whole field of stereochemistry, no more puzzling phenomena are known than those grouped under the head of the Walden Inversion, and at the present day we still await a solution of the problem. The data are so complicated that it would be impossible to deal with them fully here."[1]

From our chemical work, scientific or practical, two axioms are in general of fundamental importance; first, the stability of chemical entities under normal conditions of temperature and pressure; second, the simplicity of those chemical changes which in the case of a substitution reaction cause the direct replacement of one atom or radical by another atom or radical. The first of these axioms finds its application and confirmation in all usual processes of purification by crystallization, distillation, etc. The lifetime of pure substances is apparently long, and the permanency of chemical molecules under ordinary conditions is taken for granted. The second axiom is of importance in chemical syntheses, formulas and equations, in view of the fact that we here make use of the conceptions of directed valencies and stereochemical models.

We may ask, however, whether these axioms fit the facts. Can we show that molecules, in particular organic homeopolar molecules which undergo no ionization, exist as entities or individuals comparable in certain respects to living beings or organisms? Are they sensitive to the most delicate stimuli and external influences of their environ-

[1] Stewart, *Recent Advances in Organic Chemistry*, Vol. II, p. 16, 1927.

ment, that is, time, temperature, so-called indifferent solvents, partners in solution?[1]

One might possibly speak of an "adaptability" of these active molecules to their surroundings, or of the tendency to parallel external influences by a corresponding intramolecular rearrangement. The fact that such processes, these *actio et contractio*, are not sufficiently perceptible is the fault of our crude investigational methods.

However, such a proof is possible if we use (1) organic substances of a special constitution, that is, substances containing asymmetric atoms such as carbon, nitrogen, or sulphur, and (2) rotatory power or optical activity as a diagnostic aid with which to recognize such molecular changes.

Since a genetic relationship exists between rotatory power and chemical constitution, or, expressed in other words, between the magnitude and sign of rotatory power and the configuration of atoms in an asymmetric molecule, one may conclude that every change in rotatory power, a characteristic property of a given substance, indicates an alteration or change in the degree of asymmetry. Conversely, every rearrangement and spatial displacement of atoms in a molecule is manifested by a change in rotatory power. In general, in the rotatory power of substances we possess a physical property of widest applicability in the detection of hidden changes in organic and optically active molecules, whether or not these transformations are spontaneous or enforced, reversible or irreversible.

Influence of temperature, indifferent solvents and dissolved substances: Transient or reversible deformation of molecules.

A. l-Malic acid[2] $\begin{matrix} CHOH \cdot COOH \\ | \\ CH_2COOH \end{matrix}$

a. free acid, molten:

temperature T =	90-95°	50°	43°	40°	36°	28°
angle $[\alpha]_D$ =		−5.5°	−5.0°	−1.0°	∓0°	+0.5°	+3.0°

[1] Comp. also the multirotation and Lowry's multarotation.

[2] Walden, Ber., **32**, 2853 (1899); **38**, 371 (1905); Z. physik Chem., **55**, 44 (1905).

b. in solution:

Solvent—Water		Formic acid	Acetone
$t = 18°$ $[\alpha]_D$	$= -2.0°$	$-4.6°$ ($c = 7.66$)	-6.0
''	$=$ —	-0.75 ($c = 38.3$)	
$0°$ ''	$=$ —	$+1.1$ ($c = 38.3$)	

	Acetone and Acetaldehyde	Benzyl alcohol
$t = 18°$ $[\alpha]_D = -2.0°$	$-17.6°$ ($c = 11.8$)	$+4.0°$

B. Methyl-l-malate $\begin{matrix} CHOH \cdot COOCH_3 \\ | \\ CH_2 \cdot COOCH_3 \end{matrix}$

in free state: $(\alpha)^{20}_D = -6.86°$

In solution: methyl alcohol		acetone	benzene
t $20°$ $(\alpha)_D$	$= -8.7°$	$-11.25°$	$-2.02°$ ($c = 6.44$)
$t = 20°$ ''	$=$ ——	——	$\pm 0°$ ($c = 1.43$)
$t = 5°$ ''	$=$ ——	——	$+0.69°$ ($c = 1.45$)

In solution: methyl alcohol		chloroform	methyl alcohol +NaBr
t $20°$ $(\alpha)_D$	$= -8.7°$	$+2.93$ ($c=10$)	$(\alpha)^{15}_{gr} = +9.1$

C. Methyl-l-lactate $CH_3CH(OH)COOCH_3$[1]

Solvent:	p	$(\alpha)^{20°}_{gr}$
None	100	$+8.4°$
Water	10	$+1.4°$
Aqueous NaCl (N)	''	$+0.5°$
'' NaBr (N)	''	$+0.5°$
'' KCl (N)	''	$+0.5°$
'' NH_4Cl (N)	''	$+0.9°$
'' $CaCl_2$ (N)	''	$-1.0°$
'' $BaCl_2$ (N)	''	$-1.3°$
'' $BaBr_2$ (4−N)	''	$-9.1°$

D. l-Malic acid:

Water $[\alpha]^{20}_D = -2°$

Aqueous ammonium molybdate $[\alpha]_D = +740°$ (Gernez)

Aqueous uranyl nitrate + KOH $[\alpha]_D = -500°$ (Walden)

[1] Compare Clough, J. Chem. Soc., **113**, 529 (1918).

Influence of Time.—Racemization.

Equation: $2d \rightarrow (d + l) \leftarrow 2\,l$.

The phenomenon of autoracemization (Walden) is of interest in connection with the question of the permanency of optically active substances. Let us consider a pure organic substance, such as the dextro-rotatory bromo-

succinic ester, $\begin{matrix} CHBr \cdot COOCH_3 \\ | \\ CH_2COOCH_3 \end{matrix}$. When it is kept for some

time in a closed flask at ordinary temperatures, it undergoes spontaneous intramolecular rearrangement and a gradual decrease of the optical rotation results; in other words it *racemizes*. Several examples may be cited to illustrate this remarkable fact.

	d-bromosuccinic ester	l-bromosuccinic ester
	$t = 20°$	$t = 16–18°$
Original Sample	$\alpha_D = +55.0°$	$\alpha_D = -76.8°$
after 2 years	——	$\alpha_D = -63.5°$
after $6\frac{1}{2}$ years	$\alpha_D = +17.6°$	$\alpha_D = -24.9°$
after 11 years	$\alpha_D = +5.3°$	——

The same phenomenon may also occur in solution, as shown by the behavior of d-bromosuccinic ester:

Free ester ($c = 100$) $t = 760$; (α) fell from $+48.8°$ to $28.8°$ in 1740 minutes (29 hours)

In benzene ($c = 5$) $t = 78°$; $(\alpha)^{30°} = 61.2°$, no change in 2880 hours (4 months)

In acetone ($c = 5$) $t = 50°$; $(\alpha)^{20°}$ fell from $56.0°$ to $24.4°$ in 450 minutes ($7\frac{1}{2}$ hours).

Might we not speak of "dying molecules" much as we speak of dead catalysts? The alchemists spoke of dead metals!

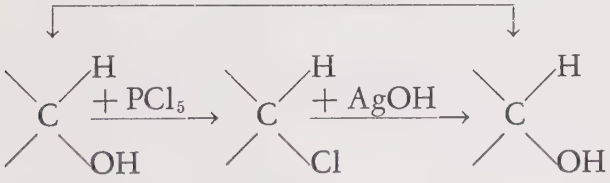
Chemical Reactions leading to stable Inversions.

Let us consider some of the simpler metathetic reactions:

(1) $R - OH + PCl_5 = R - Cl + HCl + POCl_3$
(2) $R - OH + SOCl_2 = R - Cl + HCl + SO_2$
(3) $R - NH_2 + ONCl = R - Cl + H_2O + N_2$
(chemically similar).

(4) $R - NH_2 + ONOH = R - OH + H_2O + N_2$
(5) $R - Cl + KOH = R - OH + KCl$
(6) $R - Cl + (AgOH) = R - OH + AgCl$
(chemically similar).

In general it would seem that all of these reactions of exchange are well known in all of their stages, and that the final results may be predicted. Reactions (1) and (2), or (5) and (6) should give identical products. Nothing would seem more natural than to have the exchange of atoms and radicals, one by the other, occur at the former place of linkage. Let the temperature be low, t = 0° to 50-60°, and the solvent be an indifferent substance like $CHCl_3$ (1 and 2). What happens? Consider reactions 1 (or 2) and 5 (or 6), and let us choose as the optically active substance malic acid, $HOOC \cdot CH_2 \cdot CHOH \cdot COOH$; then



We get back a malic acid. Is it the same one? Chemically, yes; stereochemically, no! It has been transformed into its optical antipode, with a directly opposite configuration. In such cases we speak of the relation of object to image, of the right hand to the left hand. Such objects are not superimposable. The effect of these reactions is, as we may express it, a complete turning "inside-out" of the molecule.

SOME EXAMPLES OF OPTICAL INVERSION

Hydroxy-Acids and Alcohols

Numerous investigations of the phenomena of optical inversion have been carried out with various types of α-hydroxy-acids (or α-amino-acids). The results which have been obtained in some of the important researches are shown in tabular form in the accompanying figures (Figs. 14–17). In the first three cases it will be noticed that the asymmetric carbon atom has *one labile hydrogen*. That this is not absolutely necessary is shown by the behavior of a

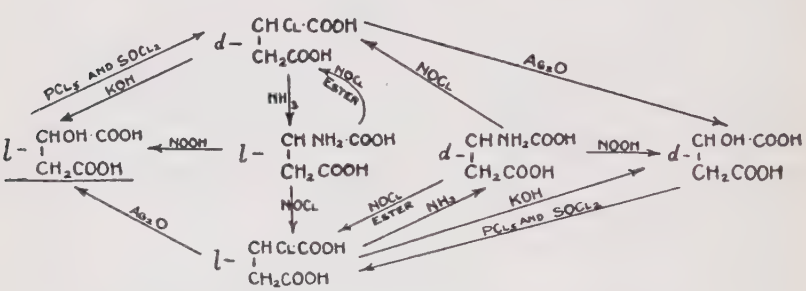


FIG. 14

The amino-acids and esters have different reactions of inversion

tertiary asymmetric carbon atom (Fig. 17), which also shows optical inversion. Examples are also given (Figs. 16 and 17) in which a *phenyl* group is attached to the asymmetric carbon atom.

It has been shown further, that optical inversion can also occur when an optically active β-hydroxy-acid is converted to the corresponding β-chloro-acid (Figs. 18 and 19). In this case the asymmetric carbon atom is also in the β-position.

Some particularly interesting examples of optical inversion have been observed in the case of certain secondary alcohols, such as phenyl methyl carbinol (Fig. 20). A number of these replacement reactions will be discussed later in connection with a consideration of the particular action of the reagents which are used to bring about the transformation.

LACTIC ACID

J. W. Walker; Th. Purdie and Williamson; Frankland and Garner; E. Fischer, Warburg and Skita.

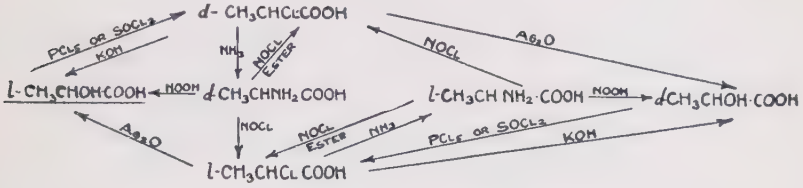


FIG. 15

The Amino-acids and Esters have different reactions of inversion

MANDELIC ACID

McKenzie, Clough and coworkers.

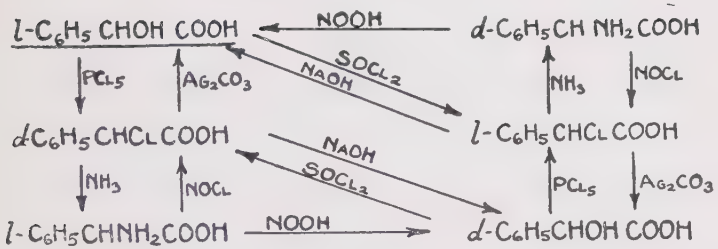


FIG. 16

The Acid and Esters show the same behavior

α-HYDROXY-α-PHENYLPROPIONIC ACID

(McKenzie and Clough)

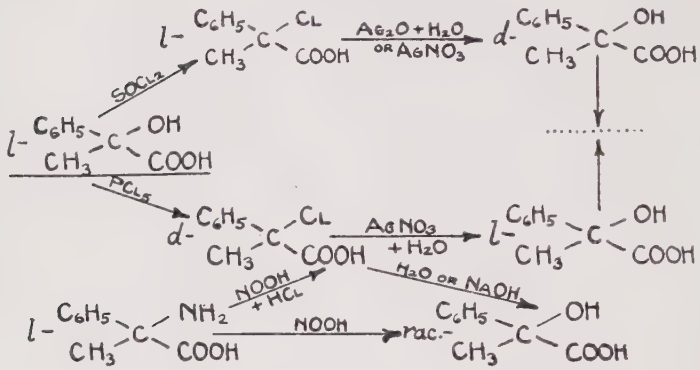

l- C6H5 CH3 C Cl COOH
Ag2O + H2O OR AgNO3
d- C6H5 CH3 C OH COOH
SOCl2
l- C6H5 CH3 C OH COOH
PCl5
d- C6H5 CH3 C Cl COOH
AgNO3 + H2O
l- C6H5 CH3 C OH COOH
NOOH + HCl
H2O OR NaOH
l- C6H5 CH3 C NH2 COOH
NOOH
rac.- C6H5 CH3 C OH COOH

FIG. 17

The Hydroxy-acids and their Esters have the same reactions of inversion

β-HYDROXYBUTRIC ACID

(E. Fischer and Scheibler)

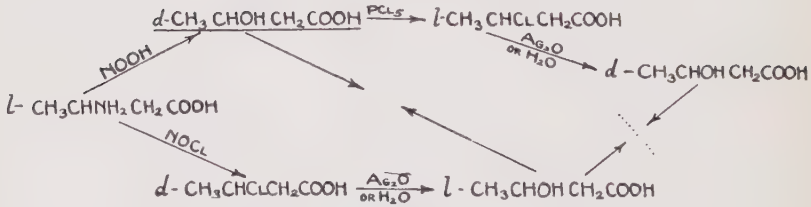


FIG. 18

The Acid and Esters have the same reactions of inversion

β-HYDROXY-β-PHENYLPROPIONIC ACID

(E. Fischer; McKenzie)

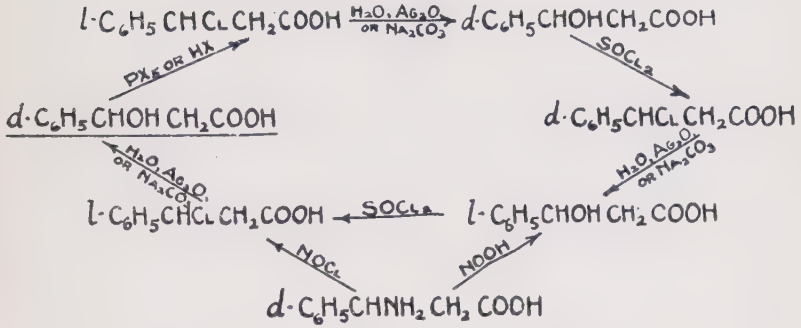


FIG. 19

The Acid and Esters react in the same manner

PHENYLMETHYLCARBINOL

(W. Marckwald; Holmberg; McKenzie and Clough)

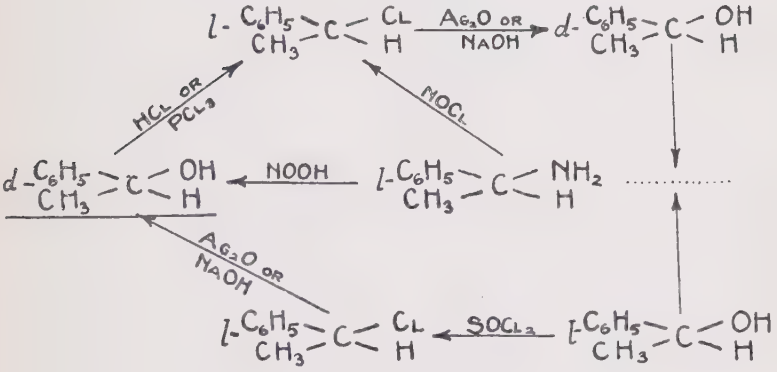
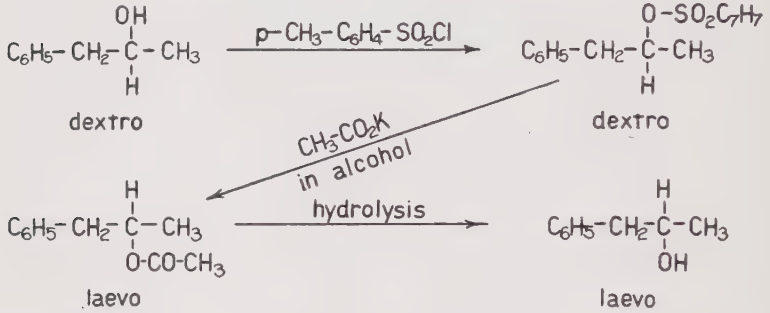


FIG. 20

Optical Inversions by means of p-toluenesulphonyl chloride.

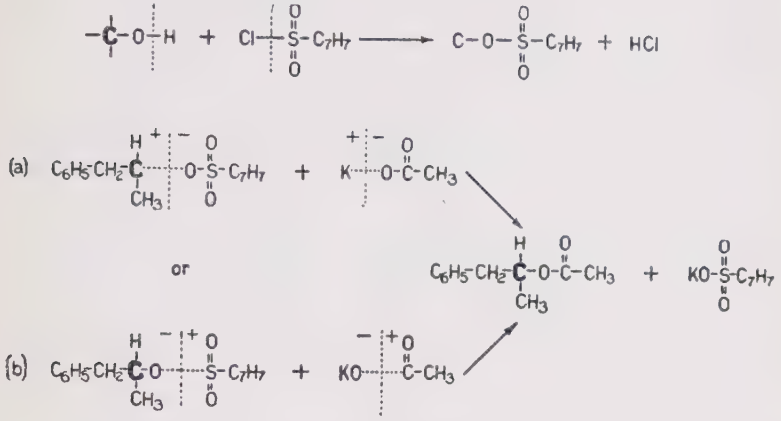
Optical inversions that are remarkable for their type and for their completeness were recently discovered by Kenyon, Phillips and Turley.[1] It was shown that the p-toluenesulphonate of *d*-benzylmethyl carbinol reacts in alcoholic solution with potassium acetate to form a *laevo*-rotatory benzylmethyl carbinyl acetate, the rotatory power of which indicates that inversion of configuration to the extent of 98.7% has taken place:



Which of these reactions caused the inversion? Did it occur in the first stage by the substitution of the p-toluenesulphonyl group? This would be an example of an inversion which does not take place *directly* at the asymmetric carbon atom; it would then take place without *rupture* of the carbon-oxygen linkage. If the inversion occurred in the second stage, resulting from the action of ionized potassium acetate, then the substitution would have occurred *directly* at the asymmetric carbon atom. One would have to assume an exchange of the $\bar{O}_2SC_7H_7$ anion by the $\bar{O}COCH_3$ anion, either by intermediate addition of the first to the active molecule, or by the intermediate liberation of the optically active cation (a).

[1] J. Chem. Soc., **123**, 44 (1923); **127**, 399 (1925).

However, still another exchange might be postulated, in which the carbon-oxygen linkage remains intact and the optically active anion (b) is formed:



Since interaction with potassium acetate takes place in alcoholic solution, and since this salt is a good conductor in this medium, it is quite probable that the ions K^+ and CH_3COO^- are present in considerable number, and that these ions take part in the reaction. Therefore it seems simpler and more probable to regard reaction (a) as the source of optical inversion. In other words, ionic exchange or direct replacement at the asymmetric carbon atom may cause a change in configuration.[1]

Figures 21 and 22 show the series of transformations involving the reactions discussed above.

Change of "Polarity" (Valency) of a Group combined with an asymmetric carbon atom.

Levene and Mikeska[2] have begun a series of experimental researches using secondary and primary alcohols in which it is sought to ascertain whether a Walden inver-

[1] Compare Lowry, Instit. Internat. de Chimie Solvay, II Conseil, 1925; Hückel, Z. angew. Chem., **39**, 842 (1926).

[2] J. Biol. Chem., **59**, 473 (1924); **60**, 1, 685; **63**, 85; **65**, 507 (1925); **70**, 355 (1926); **75**, 337, 587 (1927).

BENZYLMETHYLCARBINOL

(H. Phillips, 1923)

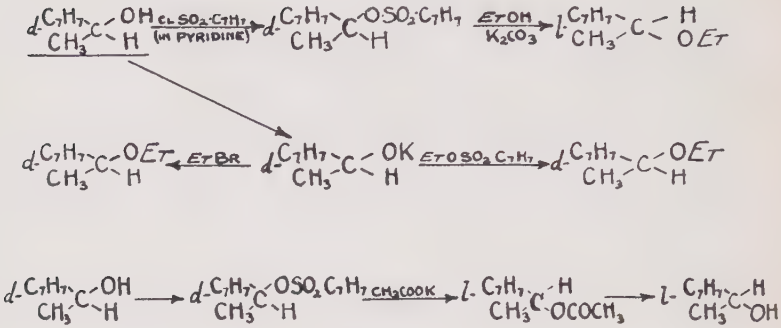


FIG. 21

LACTIC ACID

(Kenyon, Phillips, and Turley, 1925)

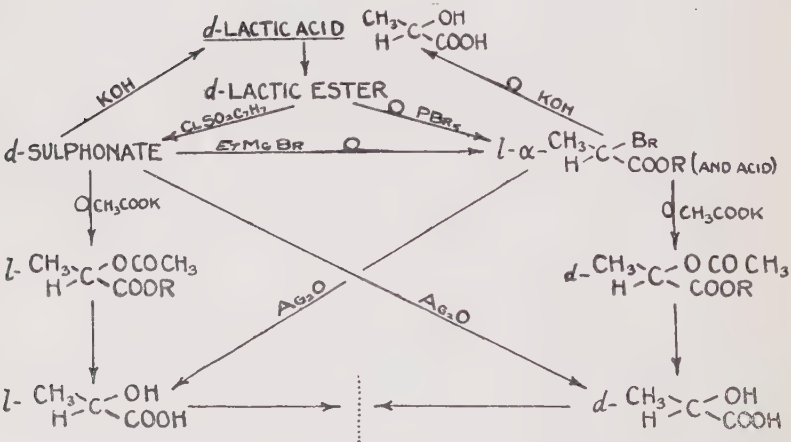
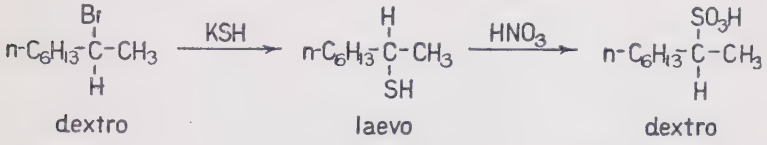
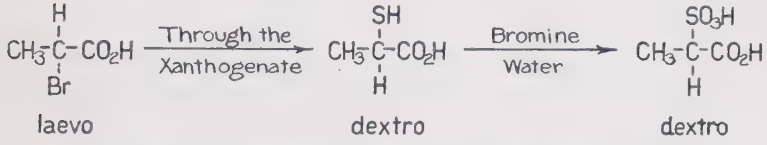


FIG. 22

sion, involving no substitution, can take place when the *polarity* of one of the four groups attached to an asymmetric carbon atom has been changed. The following examples will illustrate this problem:



A similar series of reversals of rotation occured in the ethyl, isohexyl and phenyl series.



With the thiol acids oxidation does not cause reversal of sign, with the secondary thioalcohols oxidation causes reversal of sign.

The rôle of a change of valency, by oxidation, in an optical inversion has been demonstrated in another manner in the following example (Fig. 23):

β-OCTANOL
(H. Phillips, 1925)

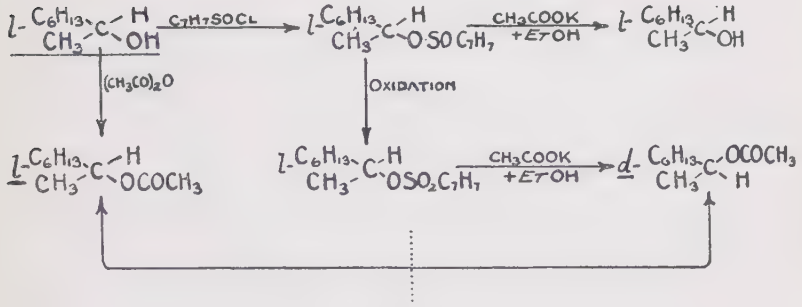


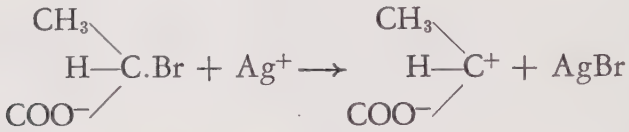
FIG. 23

The reaction of l–β–octanol, $C_6H_{13}-CHOH-CH_3$, and toluenesulphinyl chloride results in no inversion. How-

ever, change of valency by oxidation, i.e. the transformation of the sulphinyl compound into the sulphonyl, does produce an inversion.

Electric Charges acting as a Group in retaining Asymmetry.

It was Biilmann[1] who first made the suggestion that an electric charge might play the part of a group in retaining asymmetry. The action of silver nitrate on α-bromopropionic acid is thought to take place between the silver ion, Ag^+, and the acid ion:

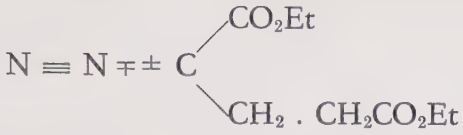


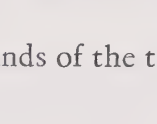
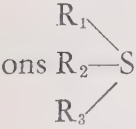
The resulting "duplex ion," $CH_3C^+H.COO^-$, is then assumed to combine with the hydroxyl ion of water to form the lactate ion, $CH_3C^+H.COO^- + \bar{O}H \rightarrow CH_3CH(OH).COO^-$. However, the argument was soon advanced that a trivalent carbon atom would suffice to form or preserve an optically active structure.[2] Therefore, it was admitted[3] that unstable combinations were formed temporarily between two "duplex ions" which were afterwards decomposed by hydroxyl ions, etc.

In recent times our views have taken another direction, and the possibility of an electric charge playing the rôle of a material radical and completing an asymmetric carbon atom has been discussed from various angles. One of the most curious cases of optical activity is that of the aliphatic diazo compounds. In 1918 Levene[4] assumed the existence of optically active diazo groups, and the occurrence of a Walden inversion in the treatment of an aliphatic amino group with nitrous acid. Chiles and W. A. Noyes[5]

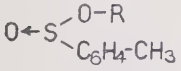
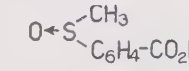
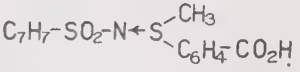
[1] Ann., **388**, 330 (1912).
[2] McKenzie and Clough, J. Chem. Soc., **103**, 687, (1913); **129**, 779 (1926).
[3] Walden, *Optische Umkehrerscheinungen*, p. 148, (1919).
[4] J. Biol. Chem., **36**, 89 (1918). Compare **21**, 345 (1915).
[5] J. Am. Chem. Soc., **44**, 1798 (1922); **42**, 2259 (1920); Ber., **57**, 1240 (1924).

obtained several optically active diazo compounds, for example, diethyl diazoglutarate, which is formulated as



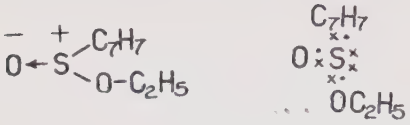
Through the investigations of Levene and Mikeska[1] the optical activity of diethyl diazosuccinate, that is, activity and asymmetry in compounds of the type  was confirmed.[2] Attention was subsequently (1924) directed to the fact[3] that the asymmetric pentavalent ammonium salts $(R_1R_2R_3R_4)NI$, as good electrolytes, are dissociated to give the optically active cation $N^+(R_1R_2R_3R_4)$. Likewise, the optically active compounds of the tetravalent sulphonium (or selenium) type, as salts, give "unsaturated" asymmetric ions  , where an electric charge seems to play the part of a group.

A special type of optically active substances has been discovered by Kenyon and Phillips, who have resolved sulphinic esters,[4] unsymmetrical sulphoxides,[5] and the sulphilimines[6] of Mann and Pope, into their optically active antipodes.

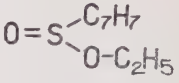




[1] J. Biol. Chem., **52**, 485, **54**, 101 (1922); **55**, 795 (1923); comp., **45**, 592 (1922).
[2] Compare also Kendall and W. A. Noyes' work on an alicyclic optically active diazo compound, J. Am. Chem. Soc., **48**, 2404 (1926).
[3] Walden, Ber., **59**, 252 (1925); Die Naturwissenschaften, 312, 331 (1925).
[4] Phillips, J. Chem. Soc., **127**, 2552 (1925).
[5] Harrison, Kenyon and Phillips, *ibid.*, 2079 (1926).
[6] Clarke, Kenyon and Phillips, *ibid.*, 188 (1927).

The existence of an optically active form of ethyl-p-toluene sulphinate, with a sulphur atom which is combined with only three different atoms and radicals, is indeed an extremely curious and important observation.



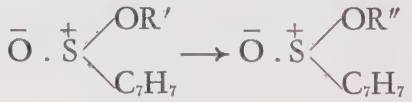
Newer Formulas



Older Formula

In the older formula the sulphur atom is written with a doubly linked oxygen; an asymmetry therefore, is impossible. The only possible formula for an asymmetric molecule is one in which the sulphur is joined to the oxygen by a single bond and this bond must be composed of the two electrons derived from the sulphur. Sidgwick[1] does not accept the views of Phillips who suggests that in every instance when a tricovalent atom has been found to act as a center of asymmetry, that atom is positively charged, either as a cation $(R)_3M^+X^-$, or as a "donor" $R_1R_2S^+ \rightarrow \bar{O}$, and he suggests that it is the presence of this charge which prevents the racemization of the molecules.

Phillips (l.c. 1925) has also brought to light a new kind of optical inversion, which he observed when esters of p-toluene-sulphinic acid undergo alkyloxy-interchange:



"the optically active ester produced has the opposite configuration to that of the original ester. The system, newly discovered, thus appears capable of undergoing a reaction which is analogous to the Walden inversion of optically active carbon compounds."

McKenzie, Roger and Wills[2] made a striking discovery when they transformed, without loss of the activity, a

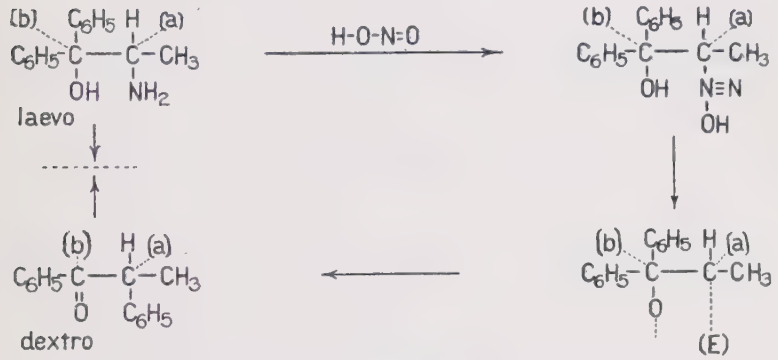
[1] Sidgwick, *The Electronic Theory of Valency*, p. 228 (1927).
[2] J. Chem. Soc., 129, 779 (1926).

levo-rotatory β-amino–α–α–diphenyl–n–propyl alcohol into an active dextro-rotatory ketone (see Fig. 24).

"During the transposition of a phenyl group (from b) to carbon atom (a) we are dealing with a reaction of substitution, the electric charge, E, playing the part of a group and being displaced by a phenyl group. . . ."

AMINO-tert.-ALCOHOL ⟶ KETONE

(McKenzie, Roger, and Wills, 1926)



("—— A Walden inversion is possible *within* the molecule itself.")

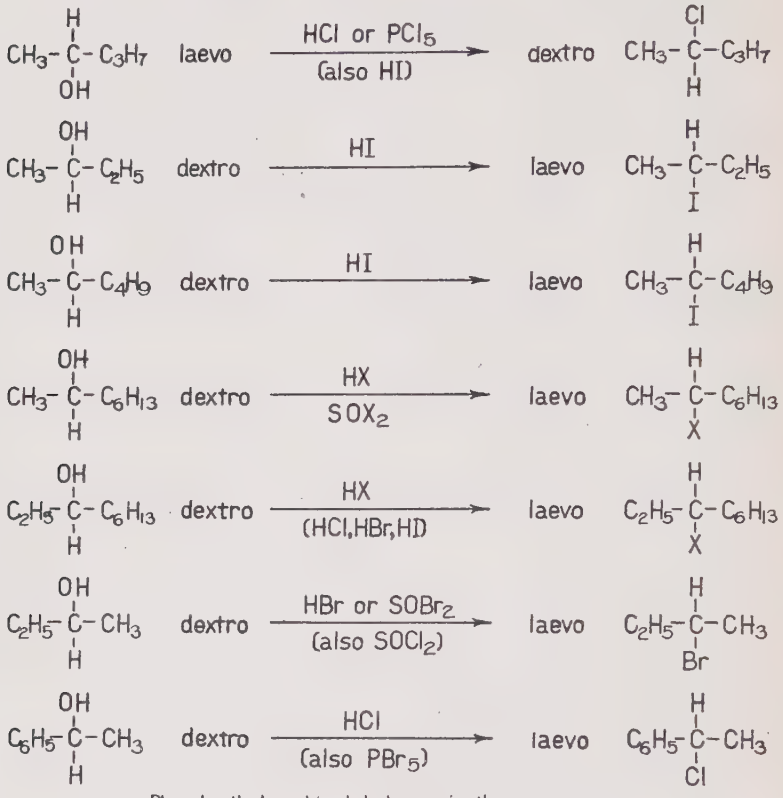
FIG. 24

Influence of the Nature of the Reactant.

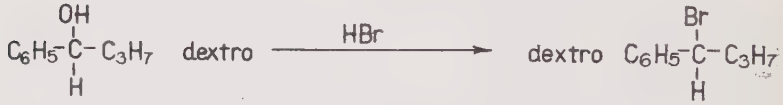
It is interesting to note that in a simple reaction, the replacement of an hydroxyl group by a halogen, we find some of our most perplexing examples of the effect of the nature of chemical reagents on optical inversion. For this simple reaction three types of halogen compounds are commonly used, hydrogen halides (HCl, HBr, and HI), phosphorus halides (PCl_3, PBr_3, PCl_5, PBr_5,) and thionyl halides ($SOCl_2$, $SOBr_2$). A number of examples of inversions in these replacement reactions are shown in the accompanying figures.

Upon examining the results obtained with numerous types of optically active compounds and a variety of halogen compounds, one is struck by the difficulty of making

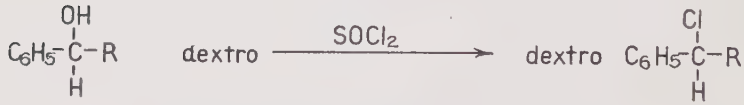
SECONDARY ALCOHOLS $\xrightarrow{\text{Halogen Acids, } PX_5 \text{ \& } SOX_2}$ SECONDARY HALIDES



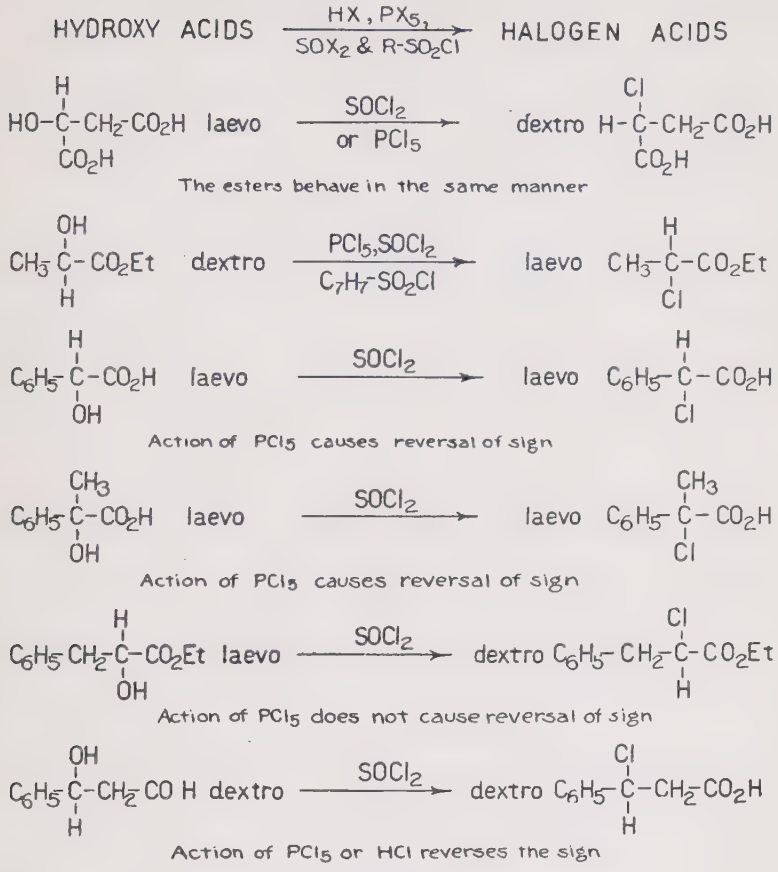
Phenyl ethyl carbinol behaves in the same manner.



Phenyl isopropyl & n-butyl carbinols behave in the same manner.



Reversal of sign is not observed in any case.
R= CH_3, C_2H_5, n-C_3H_7, iso-C_3H_7, n-C_4H_9



References:

Secondary Alcohols.—Pickard and Kenyon, J. Chem. Soc., 99, 45 (1911); Ber., **45**, 1592 (1912). Holmberg, Ber., 45, 997 (1912); McKenzie and Clough, J. Chem. Soc., **103**, 698 (1913); McKenzie and Tudhope, J. Biol. Chem., **62**, 551 (1924); Levene and Mikeska, J. Biol. Chem., **59**, 473 (1924); **70**, 355 (1926).

Hydroxy-Acids.—Malic acid: Walden and coworkers, Ber., **26**, 213 (1893); **28**, 1287, 2771 (1895); **30**, 2795, 3146 (1897); **32**, 1833, 1855 (1899).—Lactic acid: J. W. Walker, J. Chem. Soc., **67**, 914 (1895). Purdie and Williamson, *ibid.*, 69, 837 (1896). Frankland and Garner, *ibid.*, **105**, 1101 (1914). Fischer, Ber., **40**, 503 (1907).—Mandelic acid: McKenzie and Clough, J. Chem. Soc., 93, 811 (1908); **95**, 786 (1909); **99**, 1917 (1911). Kenyon, Phillips, and Turley, J. Chem. Soc., **127**, 411 (1925).—α-Hydroxy-β-phenylpropionic acid: McKenzie and Clough, J. Chem. Soc., **97**, 2564 (1910); **101**, 390 (1912).—β-hydroxy-β-phenylpropionic acid: Fischer and Scheibler, Ann., **383**, 337 (1911). McKenzie and Barrow, J. Chem. Soc., **99**, 1921 (1911).

any generalizations. McKenzie and Tudhope[1] call attention to the following facts:

(a) The extent of the displacement racemization which occurs is much greater in those cases where phosphorus pentachloride is the chlorinating agent than when thionyl chloride is used, and

(b) In every instance where the action of thionyl chloride is unaccompanied by a change of sign, there is a phenyl group in direct attachment to the asymmetric carbon atom.[2] In general, while the action of phosphorus pentachloride on an optically active hydroxy-acid or its ester is accompanied by a change of sign of rotation, the action of thionyl chloride shows a greater variation.

Influence of Concentration of the Reactant.

The studies of Holmberg,[3] dealing with the replacement of the halogen atoms of l-chloro-, l-bromo-, and l-iodosuccinic acids and their salts by the xanthogenate group and by the hydroxyl group, are of considerable importance. By varying the experimental conditions, the l-halogensuccinic acid may be converted into either the d- or l-derivative, even when one and the same chemical reaction is employed. Thus, potassium l-bromosuccinate and potassium xanthogenate in dilute solution yield l-xanthogensuccinic acid, whereas either potassium or strontium l-bromosuccinate and excess potassium xanthogenate in concentrated solution gives d-xanthogensuccinic acid. Similar results are obtained in the conversion of l-bromosuccinic acid into d- or l-malic acid, by the action of silver oxide.

The experiments of Holmberg indicate that the above reactions may occur in two ways: (a) by the direct substitution of the xanthogen or hydroxyl radical for the

[1] J. Biol. Chem., **62**, 551 (1924).

[2] Compare also Kenyon, Phillips and Turley, J. Chem. Soc., **127**, 409 (1925).

[3] J. prakt. Chem. (2) **87**, 471 (1913); **88**, 590 (1914); Arkiv Kemi Min. Geol., **6**, No. 8 (1916), Chem. Abs., **10**, 2463 (1916); No. 17 (1917), Chem. Abs., **12**, 807 (1918); No. 23 (1917), Chem. Abs., **12**, 808 (1918); Ber., **60**, 2185, 2194 (1927); Svensk. Kem. Tids., **39**, 1 (1927).

halogen; (b) by the addition of potassium xanthogenate or of water to the lactone of malic acid, which is formed as an intermediate product. This view is supported by his study of the action of silver oxide on l-bromosuccinic acid. In neutral solution silver oxide yields l-malic acid, while the use of an excess of silver oxide leads to d-malic acid. By the action of silver oxide on l-bromo or l-iodosuccinic acid under suitable conditions the intermediate product mentioned above, the free d-lactone of malic acid, may be isolated. Hydrolysis of this d-lactone acid in acid solution yields principally l-malic acid, whereas alkaline hydrolysis forms principally d-malic acid.[1]

Influence of the Solvent.

The discovery by Senter and Drew[2] that the same reagent could produce one or the other of the optical antipodes from an active material, depending upon the nature of the inactive solvent, introduced another complication in attempts to explain the Walden inversion, and gave recognition to a new important factor in the appearance of this phenomenon. Thus with ammonia, l-phenyl chloroacetic acid yields (at 9°): in acetonitrile as solvent—l-phenylamino acetic acid, in water—d-phenylamino acetic acid.

These investigators extended their experiments to other solvents and obtained in the case of the reaction of l- or d-phenyl chloroacetic acid and ammonia:

1) a *reversal* rotation: in H_2O, $C_7H_{15}OH$, $C_6H_5CH_2OH$, C_6H_5CN;

2) the *same* rotation as the original acids: in liquid NH_3, C_2H_5OH, n- and iso- C_3H_7OH, CH_3CN.

The active phenyl bromoacetic acids[3] gave upon interaction with ammonia:

[1] Analogous optical interchanges may occur in other cases where lactone or oxygen linkages enter into reaction. The determination of configuration of such products, for example in the sugar series, therefore becomes more difficult.

[2] J. Chem. Soc., **107**, 638, 908 (1915); **109**, 1091 (1916).

[3] Senter and Tucker, *ibid.* **113**, 140 (1918); see also **111**, 447 (1917).

1) a *reversal* in rotation: in water and the alcohols;
2) the *same* rotation: in liquid NH_3, in CH_3CN.
Active α-bromo-β-phenyl propionic acid[1] in all solvents gave the corresponding amino acid, phenyl alanine, with reversed rotation.

Inversion by Enzymes, "Waldenase"

Fränkel and Gallia[2] assume the occurrence of a Walden inversion by enzymes on the basis of results obtained by prolonged tryptic digestion of casein. From the very purest casein they obtained, after a 60-day period of hydrolytic action by pancreatine, a highly rotatory d-tyrosine $[\alpha]^{26}_D = +17.91°$ and a highly active d-valine $[\alpha]^{26}_D = +13.87°$. Since only l-tyrosine is obtained in the usual tryptic digestion, and since racemic tyrosine has not as yet been found among the products of prolonged action of trypsine, they concluded that the direct formation of d-tyrosine from the enantiotropic l-form had taken place as a "Walden Inversion", through the agency of enzymes. The investigators propose the name "Waldenase" for this enzyme. The following reaction occurs:

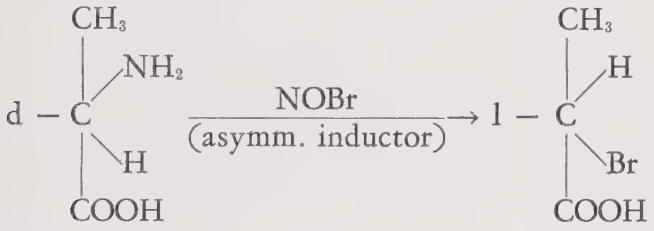
$$\text{l-tyrosine} \xrightarrow{\text{"Waldenase"}} \text{d-tyrosine}$$

It is possible that a combination between l-tyrosine and the enzyme takes place through the agency of the asymmetric carbon atom. In such a case, a regrouping into the d-form by subsequent hydrolysis is just as possible as in the other instances of the Walden inversion. The existence of an enzyme of this kind or of such enzyme activity is important in respect to the degree of certainty with which conclusions as to the configuration of the *original* substances may be made on the basis of the optical character of decomposition products formed by enzymes. Such conclusions become rather doubtful if we assume the possibility of the common occurrence of such inversions by enzymes.

[1] Senter, Drew and Martin, J. Chem. Soc., **113**, 151 (1918); *ibid.*, **125**, 2439 (1924); **127**, 1847 (1925).
[2] Biochem. Z., **134**, 308 (1922).

Asymmetrical Induction.

Erlenmeyer[1] assumed the existence in asymmetric molecules, of a power comparable to a magnetic form of energy which acts inductively upon optically inactive substances. By such "asymmetrical induction" he claims to have prepared an optically active form of cinnamic acid, C_6H_5CH: CH.COOH, and of benzaldehyde[2], C_6H_5CHO, by melting these substances with tartaric acid. He explains the "Walden Inversion"—if it takes place—by the asymmetric influence, during chemical interaction, of the undecomposed part of the optically active primary substance, i.e.



SOME RECENT THEORIES CONCERNING THE "WALDEN INVERSION"

With reference to the "Walden Inversion" Lewis[3] says: "There seems to be but one possible way of accounting for this peculiar behavior. Let us consider a carbon attached to the four radicals R_1, R_2, R_3 and R_4, and let us assume that a fifth group R_5 becomes temporarily attached to the carbon atom near to the face of the tetrahedron which is opposite to R_1. A slight shift of the kernel might make it now the center of a new tetrahedron with corners at R_2, R_3, R_4, and R_5, while R_1 would become detached from the molecule. Then if the radical R_5 in the new molecule were to be replaced by the radical R_1, the resulting

[1] Biochem. Z., **97**, 255 (1919), **103**, 79 (1920); **133**, 52 (1922). Compare also Lowry and Walker, Nature, **113**, 565 (1924).

[2] Compare the experimental work of Wedekind, Ber., **47**, 3172 (1914), and Erlenmeyer, Biochem. Z., **66**, 509 (1914).

[3] *Valence and the Structure of Atoms and Molecules*, p. 113, (1923).

molecule would be the mirror image of the one with which we started. In this explanation it is not necessary to assume that the five radicals are attached to the carbon for any appreciable period of time, indeed it might be assumed that the R_1 leaves at the same instant that R_5 becomes attached to the carbon atom." This explanation would assume the intermediate existence of a compound containing pentavalent carbon.

Lowry[1] makes the following suggestion:

I. The carbon atom has two stable configurations, namely a *tetrahedral* form in neutral atoms, which easily passes into a *triangular* configuration when the atom is positively charged, but reverts to the tetrahedral configuration when this charge is neutralized.[2]

II. Since the Walden inversion appears to be limited to an exchange of anions, it is necessary to admit that the asymmetric carbon atom must assume, at least momentarily, the form of a cation. Consequently a "normal" substitution implies the neutralization of this positive charge by an anion which replaces the former anion directly, on the same side of the plane of the cation C^+PQR.

III. A change of configuration (optical inversion) will occur if two negative radicals X and Y are attached simultaneously to opposite sides of the plane which contains the positive radical C^+PQR, giving rise to an intermediate complex, such as illustrated in Fig. 25.

Kenyon, Phillips and Turley[3] have developed a theory which may be illustrated by taking ethyl α-bromopropionate as an example. If we suggest that the reactive atom of the halogen compound exerts its residual affinity in the

[1] Instit. Internat. de Chimie Solvay, II Conseil (1925).

[2] Compare tetrahedral C in diamonds and all quadrivalent carbon atoms. Triangular or planar in the carbonate ion, $O^- - C^+(O^-)(O)$ in calcite (Bragg, 1914), and in acetate ion $CH_3 - C^+(O^-)(O^-)$ in basic beryllium acetate (Bragg, 1923).

[3] J. Chem. Soc., 127, 406 (1925).

direction of the α-hydrogen atom and in this way causes the carbon atom to become unsaturated, then the interaction with the salts of the alkalies can be indicated

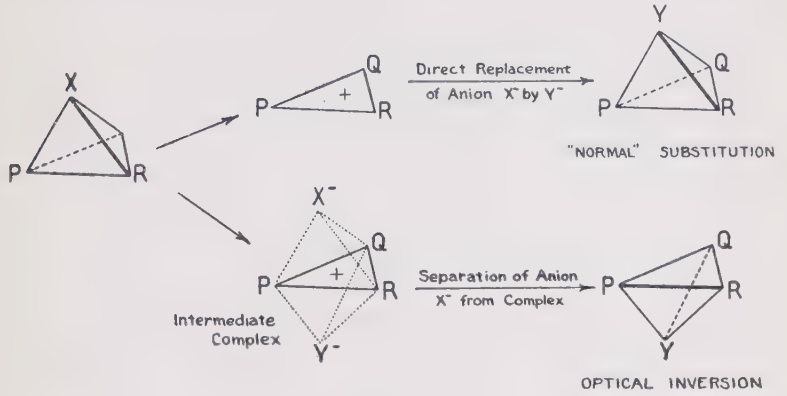
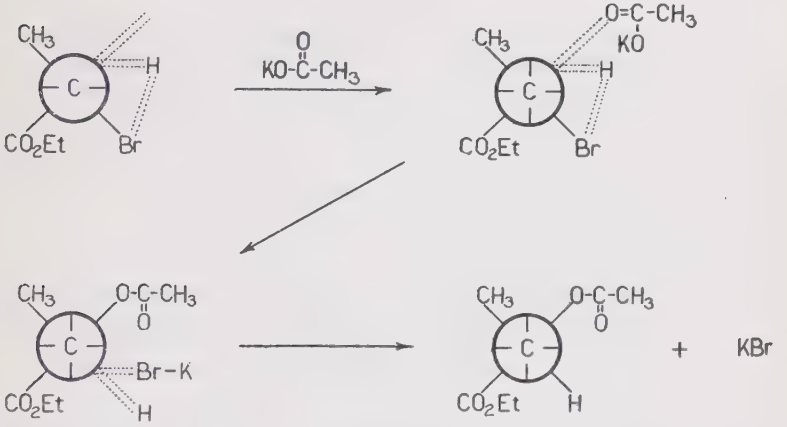


FIG. 25

in the following stages in the gradual transition of an ethyl α-bromopropionate molecule into ethyl acetoxypropionate by interaction with potassium acetate, CH_3COOK.



An inversion of the configuration of the molecule will result. Similarly, a direct reaction without inversion can be postulated, passing through a gradual series of changes.

Meisenheimer[1] has recently been occupied with the nature of chemical reactions which lead to an optical inversion. He would interpret three reactions from a common point of view, namely: "(1) the Walden inversion, (2) an abnormal substitution reaction often observed in the case of unsaturated alcohols, chlorides, etc., and (3) the *trans*-addition to ethylene compounds. Every attempt to describe the process of substitution on a saturated carbon atom must take into account the Walden inversion. Optical inversion phenomena, observed in the case of asymmetric carbon atoms, have taught us that the old idea of the nature of substitution—direct replacements of atoms or groups of atoms by others—is not always correct."

To explain these facts, Meisenheimer assumes in the first place, that valencies do not represent definitely directed forces, but that the position of the substituents surrounding the central atom as well as the linking of the electrons negotiating their combination, are dependent upon mutual attraction and repulsion; furthermore, that substitution does not involve addition to the central atom, but involves previous attachment to the atoms which is to be replaced. This weakens the bonds of the latter and the other atoms attached to the carbon atom suffer a simultaneous change in affinity relationships. A new affinity residue on the carbon atom becomes existent, and this makes possible another attachment. Meisenheimer illustrates this by the reaction (Fig. 26) involving replacement of chlorine by hydroxyl by means of potassium hydroxide. The approach of the positive potassium in KOH to the negative chlorine causes formation of the addition product (I) and distortion of the methyl chloride tetrahedron. The displacement of the chlorine atom away from the carbon atom enhances the positive character of the latter, and this in turn attracts a second molecule of KOH so that its electronegative constituent, oxygen, is attached to the carbon atom (II). Decomposition of the addition product

[1] Ann., 456, 126 (1927).

(I) produces a direct replacement, whereas (II) gives a product in which a change of position has taken place. It is impossible, however, to predict *a priori* whether or not any particualr reaction will lead to a Walden inversion.

It seems that in general, the theories of Lewis, and of Kenyon, Phillips and Turley, as well as that of Meisenheimer, make use of a common principle—"residual affinity"—and formation of more or less stable intermediate

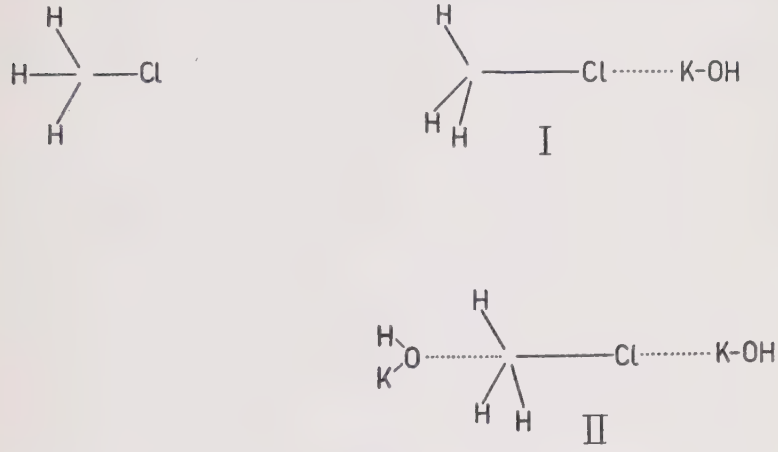


FIG. 26

addition compounds, which can or cannot produce an inversion of the configuration. Moreover, it must be remembered that the reagents employed—potassium acetate and potassium hydroxide, strong electrolytes in alcoholic (or aqueous) solutions—are ionized. Therefore all interpretations of these reactions of substitution must take into consideration the *ions* of these electrolytes and not merely the molecules.

SUMMARY

A. The immediate and practical result of the discovery of "optical inversion" was that it opened a way for transforming a given optically active substance into its antipode without the necessity of previous racemization, and then resolving the racemic compound according to

Pasteur's classical methods. Emil Fischer therefore said in 1907, "This discovery is the most surprising observation in the field of optically active substances since the fundamental investigations of Pasteur."

This discovery exerted a profound influence upon certain theoretical questions concerning both the configuration of molecules and, in general, the nature of substitution reactions.

B. I. The "optical inversion" has clearly shown that an optically active body and an optically active derivative prepared from the former by simple reactions, need not, *eo ipso*, both possess the same configuration. It therefore follows that,

II. The conception of four carbon valencies as rigidly directed forces in space can no longer be supported. The tetrahedron model of the carbon atom with its four atoms or radicals combined in definite positions in space represents but one limiting case, a condition which might possibly arise in the solid state, or at absolute zero, or where the constitution is of a very accentuated homeopolar character.

III. The process of substitution would not necessarily consist of the simple interchange of an atom or a radical for another. It would much rather seem to be a series of reactions, taking place in several steps and involving valence changes, intermediate action and the formation of intermediate products.

IV. The chemical nature of the reactants, their concentration as well as the chemical nature of the solvent, all have a more or less pronounced effect upon reactions involving the substitution of a given individum. Thus far, an exact functional dependency upon all these variables is lacking.

V. "The Walden inversion seems to be a general phenomenon which stands in intimate relationship to the nature of substitution processes."[1] Therefore "every description of a substitution reaction involving linkage to a

[1] E. Fischer (1911).

carbon atom must take the Walden inversion into account." (Meisenheimer).[1]

VI. "It seems justifiable generally to emply the originally coined terminology, "Walden Inversion," for all substitution reactions where the new substituent does not take the place of the previous one."[2]

VII. The Walden inversion casts some doubt upon the truth of the stereo-isomeric relations of the complex metal ammonates.[3] According to Werner, substitution reactions in the cis-form should give a cis-configuration and a cis-compound, and a trans-form should give a trans-compound. This is, however, not absolutely necessary.

VIII. In general it may be permissible to say that in all substitution reactions involving polyvalent atoms (for example, carbon, sulphur, nitrogen, and certain metals) the new substituent need not necessarily enter in the same position occupied by the atom or radical which is being replaced, but may occupy another valence position. May not such a shift also take place in transient addition and decomposition reactions. What about the optical mutability of decomposition reactions brought about by mild oxidation or hydrolysis as in the case of the sugars or carbohydrates, the proteins, alkaloids? Must not a similar inversion be taken into account if we assume synthetic and decomposition reactions to take place in living cells through the agency of enzymes?

IX. Substitution processes on asymmetric and optically active carbon atoms represent particularly favorable cases for study, since the property of optical rotation places easily recognizable means for the determination of changes of position at the disposal of the investigator. Perhaps the use of optically active substances, in combination with inactive substitution products, might afford a method for the detection of spatial changes in the latter.

X. Frankland's opinion (1913) respecting the significance of optical inversion would therefore seem to be

[1] Meisenheimer, Ann., **456**, 126 (1927).
[2] Hückel, Z. angew. Chem., **39**, 842 (1926).
[3] Reihlen, Z. anorg. Allgem. Chem., **159**, 347 (1927); Ann., **447**, 211, 448, 312 (1926).

correct. "It is highly probable that it (i.e. Walden's discovery) may mark an epoch in our views with regard to the mechanism of the process of substitution in general."

C. Optical inversion has acted as an important scientific catalyst in the field of experimental investigations on optically active substances and their substitution products. Among the outstanding investigators in this field are, Emil Fischer and his coworkers, McKenzie and his colleagues, Clough, Drew, Wren and Senter, Purdie, Frankland, Pickard, Kenyon, Phillips, Holmberg, Darapsky, Lutz, Werner and his successor Karrer, W. A. Noyes, Levene and Mikeska, Kuhn, Fränkel, Meisenheimer, Freudenberg and others. One of the most successful investigators in this field is C. S. Hudson.[1] These workers were creative and instrumental in discovering new kinds of optically active substances and new types of optical inversions.

D. Resulting from work on the inversion itself, a great number of new facts has been brought to light, and a new theoretical stimulus has been given to research in rotatory power, in particular to rotation dispersion and its dependency upon temperature, source of light and solvent.

But what causes optical rotation and what asymetric arrangement of electrons is required to produce it? Which special electronic orbits must be present? What is the relationship between the numerical extent of the rotation and the physical and chemical properties of the elements or radicals linked to the asymmetric atom? In general, what is or what must be the construction of an optically active (asymmetric) atom from the modern point of view?

E. Finally, chemical theory and scientific speculation in general were stimulated to a remarkable degree by this discovery. An explanation, a theoretical basis, was necessary for this new group of facts which ran contrary to all current theoretical ideas.

Actually, the reality has surpassed all expectations. Up to the present time no less than twenty-five theories

[1] *Relations between rotatory power and structure in the sugar group, Part I*, U.S. Bur. Stds. Sci., paper No. 553 (1926).

have been advanced to explain this phenomenon. The discoverer of this inversion has had the unusual honor of seeing the most influential men gathered around his "brain child." They have bestowed gifts upon this child, and many of them have proposed chemical or physical theories to explain the nature of this phenomenon. Although in the meantime this child has grown up, and has reached the age of thirty years, chemists who are studying the configuration of molecules still regard it as an *enfant terrible*. Although many suggestions have been advanced to explain the phenomena grouped under the "Walden Inversion," a completely satisfactory solution has not yet been attained nor has it been found possible to predict the course of an inversion.

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